

3. The basic processes: adsorption and desorption, surface reactions

3.1. Thermodynamics and kinetics of adsorption and desorption

The chemist is aware of the synergetic effects arising from a simultaneous application of thermodynamic and kinetic concepts. To give a few examples, the (thermodynamical) Langmuir adsorption isotherm has a simple kinetic derivation, basing on the assumption of a dynamical equilibrium [La18]. We evaluate adsorbate binding energies from the temperature-dependence of desorption rates [Re62], whereas the basic assumption of the transition state theory (TST) is that of an equilibrium between reactants and activated complex, treated with statistical thermodynamics [Ey35, Gl41, Ey44]. In the following, we outline some basic concepts of surface thermodynamics and kinetics which are important for this work and try to emphasize the close relationship between them.

ISOSTERIC HEAT OF ADSORPTION – The temperature-dependence of the adsorption/desorption equilibrium pressure can be described by the Clausius-Clapeyron equation. This equation defines different isothermal heats of adsorption depending on which of the parameters are kept constant. Experimentally it is often convenient to fix the coverage, $\Theta = n_A/n_S$ (with the number of adsorption sites, n_S , and the number of adsorbate particles, n_A). In this case, the differential equilibrium condition between adsorbate and gas phase, $d\mu_S = d\mu_G$ (with the chemical potential of the gas phase, μ_G , and of the condensed phase, μ_S) leads, by neglectation of the volume of the condensed phase, to:

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_\Theta = \frac{Q_{st}}{R} \quad (\text{Eq. 3.1})$$

Eq. 3.1 describes adsorption isosters and defines the isosteric heat of adsorption, Q_{st} , which is the negative partial molar adsorption enthalpy¹, i.e.,

$$-Q_{st} = \left(\frac{\partial h_{ads}}{\partial n} \right)_{p,T} - \left(\frac{\partial h_g}{\partial n} \right)_{p,T} \equiv H_{ads} - H_g = \left(\frac{\partial \Delta_{ads}h}{\partial n} \right)_{p,T} \equiv \Delta_{ads}H \quad (\text{Eq. 3.2})$$

with the partial molar enthalpies of the gas phase, H_g , and of the adsorbate, H_{ads} , and the adsorption enthalpy, $\Delta_{ads}h = h_{ads} - h_g$.

¹ Uppercase letters denote partial molar quantities, lowercase letters extensive quantities. This notation is applied throughout this work. The indices 'g' and 'ads' indicate gas and adsorbed phase, respectively.

Clark [Cl70] showed that there is no limit to the number of heats of adsorption which can be expressed in terms of equations of the Clausius-Clapeyron type, depending on which state function is fixed.

Eq. 3.1 can be employed for evaluating Q_{st} as a function of coverage from experimental data. For this purpose, we fixed certain pressures, p_i , in the gas phase, varied slowly the temperature and measured the corresponding equilibrium coverages by monitoring the adsorbate-induced work function change, $\Delta\phi(\Theta)$ (see Sections 4.3 and 8.5). This procedure leads to adsorption isobars, $\Theta_{p_i} = \Theta_{p_i}(T)$, which can be rearranged to data triples $(p, T, \Theta)_i$. From these triples we obtained, by applying Eq. 3.1, $Q_{st}(\Theta_i)$ from the slope of a linear plot of $\ln p(\Theta_i)$ vs. $1/T(\Theta_i)$. This procedure can be repeated for all coverages Θ_i of interest.

A relation between Q_{st} and the adsorbate binding energy, E_0 , follows from equipartition considerations. In the case of a monatomic gas, the enthalpy of the gas phase is $H_g = U_g + pV_g = (5/2) RT$. For estimating the enthalpy of the adsorbate phase, H_{ads} , we must distinguish between mobile and localized adsorption. For mobile adsorption, free translations are restricted to two dimensions ($= RT$), but there is one vibrational degree of freedom (DOF) normal to the surface ($= RT$), so that $H_{ads} = U_{ads} = -|E_0| + 2 RT$. With Eq. 3.2, we get $Q_{st} = |E_0| + (1/2) RT$. In contrast, localized adsorption leads to three vibrational DOFs ($= 3 RT$), and the isosteric heat amounts to $Q_{st} = |E_0| - (1/2) RT$. Thus, Q_{st} is always close to $|E_0|$ within $\pm (1/2) RT$, if we assume that all adsorbate-substrate vibrations are fully excited. The same considerations, applied to the case of a diatomic molecule, yields $Q_{st} = |E_0|$ for mobile and $Q_{st} = |E_0| - (3/2) RT$ for localized adsorption.

If adsorption proceeds in equilibrium, the adsorption entropy, ΔS_{ads} , and, thus, the partial molar entropy of the adsorbate, S_{ads} , can be deduced from Q_{st} :

$$\Delta S_{ads} \equiv S_{ads} - S_g = S_{ads} - \left\{ S_g^0 - R \ln \frac{p}{p^0} \right\} = -\frac{Q_{st}}{T} \quad (\text{Eq. 3.3})$$

(with the standard gas phase entropy $S_g^0 = S_g(p^0)$ at the standard pressure p^0).

Information about the configuration of the adsorbate layer is provided by a comparison of experimental and theoretical entropies. The theoretical values can be derived from the partition functions, which contain information about the degrees of freedom available to the adsorbed particles and, thus, about the thermodynamical state of the adsorbate. A concise treatment of this topic is given in Ref. [Cl70], an application to CO adsorption on gold in Section 8.5 of the present work.

ADSORPTION ISOTHERMS – Instead of measuring adsorption isobars, we may just as well fix the temperature, T_i , and vary p , or we can rearrange the triples $(p, T, \Theta)_i$ in order to get adsorption isotherms, $\Theta_{T_i} = \Theta_{T_i}(p)$. A theoretical adsorption isotherm was first derived by Langmuir [La18] under the following assumptions: (a) the adsorption is localized, (b) the surface is saturated at $\Theta = 1$ ML (monolayer), (c) the adsorbate molecules do not interact, (d) all adsorption sites are equivalent. The rates of adsorption, R_{ads} , and desorption, R_{des} , are given by:

$$R_{\text{ads}} = k_{\text{ads}} p (1 - \Theta)^n \quad \text{and} \quad R_{\text{des}} = k_{\text{des}} \Theta^n \quad \text{with } n = 1, 2, \dots \quad (\text{Eqs. 3.4 and 5})$$

Applying the dynamical equilibrium condition, $|R_{\text{ads}}| = |R_{\text{des}}|$, we obtain:

$$\Theta_n = \frac{(b_n p)^{1/n}}{1 + (b_n p)^{1/n}} \quad \text{with } b_n = b_n(T) = k_{\text{ads}}/k_{\text{des}}. \quad (\text{Eq. 3.6})$$

The comparison with a thermodynamically derived Langmuir isotherm allows the interpretation of the constant b_n [Vo25, Fo35].

A modification of the Langmuir isotherm that considers adsorbate interactions is the Tempkin-Pyzhev isotherm [Te40]. It has the same form as Eq. 3.6, but the coefficients b_n are assumed to be coverage-dependent, $b_n = b_n(T, \Theta)$. The similar Fowler isotherm was derived with a different formalism [Fo35]. Adsorption on inequivalent adsorption sites is well treated by the (empirical, but later theoretically derived) Freundlich isotherm [Fr09]. The BET (Brunauer, Emmett, and Teller) isotherm bases on the same assumptions as the Langmuir isotherm, but it considers also multilayer adsorption [Br38]. It is mainly used for the determination of the specific surface area of powder samples. Other approaches derive adsorption isotherms from the adsorbate phase behaviour. Most important are the lattice gas models [Fo35, Hi52], for which exact and Monto-Carlo solutions were reported [Ma96]. Approximate solutions for adsorption isotherms which consider adsorbate interactions include the Bragg-Williams or mean field approximation [Br34], which provides an isotherm that is equivalent to Fowler's, the Bethe-Peierls approximation [Be35, Pe36], and the quasichemical approximation (see [Ma96]).

In Eq. 3.5, the (THERMAL) DESORPTION RATE, R_{des} , is described by a rate law of the order n . If we apply the Arrhenius equation to the rate constant, k_{des} ,

$$R_{\text{des}} = k_{\text{des}} \Theta^n = v_n \exp\left(-\frac{E_{\text{des}}}{RT}\right) \Theta^n \quad (\text{Eq. 3.7})$$

then the resulting equation 3.7 is referred to as Polanyi-Wigner equation [Hi58]. Eq. 3.7 is the basis for the interpretation of thermal desorption spectra (see Section 4.1) and defines the desorption activation energy, E_{des} , and the frequency factor of desorption, ν_n .

A theoretical interpretation of the rate constant k_{des} is provided by the transition state theory (TST) [Ey35, Gl41, Ey44]. The TST postulates that the reaction rate is proportional to the concentration of the activated complex, which corresponds to the state of maximum energy on the reaction path, the transition state. The concentration of the activated complex is calculated with the tools of statistical thermodynamics by assuming a chemical quasi-equilibrium between reactants and activated complex. This treatment leads to the famous Eyring equation:

$$k_n = \kappa \frac{k_B T}{h} \frac{Q_{-\text{vib}}^\ddagger}{Q_{\text{ads}}^n} \exp\left(-\frac{E_{\text{des}}}{RT}\right) \equiv \kappa \frac{k_B T}{h} K_{-\text{vib}}^\ddagger, \quad (\text{Eq. 3.8})$$

which contains the partition functions of the transition state, $Q_{-\text{vib}}^\ddagger$, and of the adsorbate, Q_{ads} , and the transmission coefficient, $\kappa \leq 1$. Eq. 3.8 also defines the quasi-equilibrium constant $K_{-\text{vib}}^\ddagger$, which is the key for the thermodynamical interpretation of the TST. With the relation between $K_{-\text{vib}}^\ddagger$ and the standard Gibbs activation energy, ΔG_\ddagger° ,

$$\Delta G_\ddagger^\circ = \Delta H_\ddagger^\circ - T\Delta S_\ddagger^\circ = -RT \ln K_{-\text{vib}}^\ddagger, \quad (\text{Eq. 3.9})$$

we obtain:

$$k_n = \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S_\ddagger^\circ}{R}\right) \exp\left(-\frac{\Delta H_\ddagger^\circ}{RT}\right). \quad (\text{Eq. 3.10})$$

With Eq. 3.10, standard desorption activation entropies, ΔS_\ddagger° , and enthalpies, ΔH_\ddagger° , can be deduced from experimental rate constants. Transition state theory is frequently used in this work for the interpretation of desorption frequency factors; an extensive discussion can be found in Section 6.7.

3.2. Physisorption and Chemisorption

Creating a surface means to cleave a large number of bonds: the ubiquitous van der Waals bonds and, depending on the material, covalent, metallic, and ionic bonds. The resulting free valences lead to a high surface energy, which can be lowered by surface relaxations

and reconstructions. All surfaces undergo relaxations, reconstructions only a few. Typical examples for the latter are the 1×2 reconstructions of the (110) surfaces of the metals Pt, Ir, and Au² or the 7×7 reconstruction of the (111) surface of the covalent Si crystal. Reconstructions allow a partial saturation of the free valences, especially in the case of covalent solids. The remaining free valences are responsible for the occurrence of adsorptive forces.

PHYSISORPTION – If the adsorptive bond is only due to van der Waals interactions, as usual in the case of noble gas adsorption, we speak of physisorption, which is the weakest form of adsorption with typical binding energies between ≈ 2 kJ/mol ($\text{H}_2/\text{W}(111)$ [Ch93]) and 29 kJ/mol ($\text{Xe}/\text{Ru}(10\bar{1}0)$ [Sc02]). A simple description of the van der Waals interaction between a solid and an atom is provided by London's harmonic oscillator model applied to a hydrogen atom interacting with its image in a perfect conductor [Za88]. This approach leads to the following expression as a first approximation of the total electrostatic energy:

$$U = -\frac{1}{8} \frac{e_0^2 r^2}{z^3} \quad . \quad (\text{Eq. 3.11})$$

The numerator is formally the product of two dipole moments – one for the atom and one for its image. The fact that U is proportional to the square of the radius of the electron orbit in the H atom, r , accounts for the fact that large atoms are more effectively attracted than small. Furthermore, U is inversely proportional to the cube of the distance between the atom's centre and the surface, z . The power of z differs from that of the common expression for the attractive van der Waals term, which is $\propto z^{-6}$, but equals that of the interaction energy between two permanent, fixed dipoles. It can be shown that the usual z^{-6} term arises from a Boltzmann-statistically weighted averaging over all more or less favourable orientations of two rotating dipoles. We obviously obtain a z^{-3} term for the atom-surface van der Waals interaction, because the oscillating dipole, the H atom, and its image in the conductor are always in phase, i.e., in a relative orientation of minimum energy. A further expansion of the power series, of which Eq. 3.11 provides only the leading term, reveals that the substrate induces a permanent dipole moment in the adsorbed atom if it is brought close to the surface. Quantum-mechanically, this dipole moment is due to a mixing of excited states of the adsorbed particle with substrate states. LDA³

² Cf. Section 2.1.

³ Local density approximation of the full density functional theory. In LDA, the exchange-correlation energy density of each infinitesimal region of the inhomogeneous electron distribution is approximated by the respective value for a homogeneous electron gas of the same density. The calculation of the latter is straightforward. LDA is often applied to surfaces and adsorption systems.

calculations, for example on Xe/jellium, confirm this permanent polarization and predict an electron charge accumulation between atom and surface [La81, La82]. The latter is probably responsible for the large negative work function change caused by physisorbed particles.

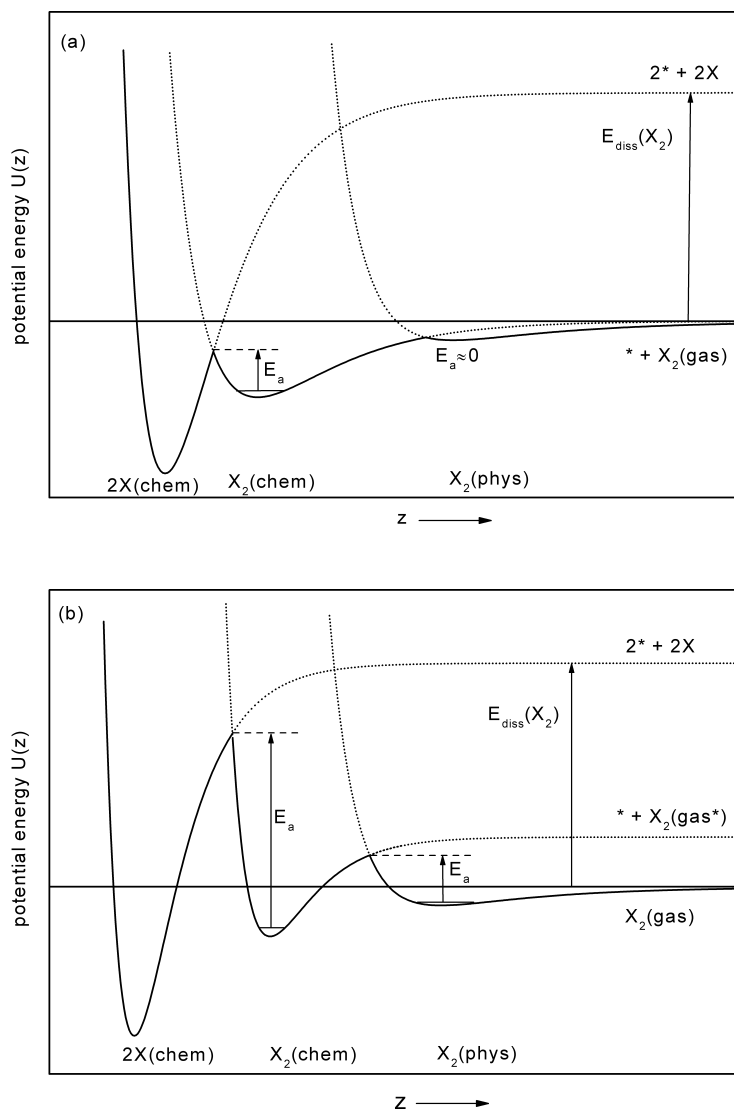


Fig. 3.1: Schematic potential energy curves for a homonuclear, diatomic molecule X_2 approaching a metal surface.

(a) Molecular chemisorption and dissociation only weakly activated. Typical of O_2 adsorption on most transition metals. z is the coordinate of the minimum energy path on the potential energy surface of the X_2 molecule approaching the surface. On this path both the intermolecular distance $d(X-X)$ and the X_2 -surface distance vary. Otherwise the $X_2(\text{chem})$ curve would not necessarily converge to zero for $z \rightarrow \infty$ (as it is the case in (b)).

(b) Molecular chemisorption and dissociation substantially activated. Example: O_2 adsorption on gold surfaces. In this figure, z is the X - or X_2 -surface distance with $d(X-X)$ fixed at the equilibrium value of the adsorbed molecule. This interpretation of z is more suitable for visualizing the activation barrier for molecular chemisorption. Accordingly, $X_2(\text{gas})^*$ is the gas phase molecule with the same intramolecular distance $d(X-X)$ as in $X_2(\text{chem})$.

CHEMISORPTION – In contrast to physisorption, chemisorption is characterized by the formation of a covalent chemical bond between adparticle and surface with typical dissociation energies > 30 kJ/mol. If the adparticle is a molecule, then changes of the orbital energies may lead to an occupation of anti-bonding levels, resulting in a spontaneous dissociation. Fig. 3.1 shows the respective potential energy curves for adsorption of a diatomic molecule. On the Au(110) surface, dissociation of all molecules investigated in this work (see Section 2.2) proved to be substantially activated. However, we succeeded to generate e.g. chemisorbed atomic oxygen by electron-impact activation of physisorbed O_2 molecules.

3.3. Surface reactions

The effect of a solid catalyst is to enable a surface reaction as a faster alternative to a gas phase (or solution) reaction. The reactions steps of composite reactions and the intermediates are often similar for both ways of reaction. The major difference between gas phase and surface reaction consists in the free energy of the intermediates, which is usually lower on the surface. As a result, the rates of surface reactions are often higher – this is the catalytic effect. The relevant literature [An81, Ki82, Ma94, Ma96] distinguishes between three generic types of surface reactions depending on the mechanism: (i) the Langmuir-Hinshelwood (LH) reaction, (ii) the Eley-Rideal (ER) reaction, and (iii) the precursor-mediated (PM) reaction.

We consider a reaction $A + B \rightarrow AB$. In the LH mechanism, both reactants A and B adsorb. The adsorbed species A_{ad} and B_{ad} react on the surface forming $(AB)_{ad}$, which finally desorbs. In the ER mechanism, only A adsorbs and then reacts with an incoming B to give an adsorbed AB_{ad} . This species finally desorbs. In the PM mechanism, species A adsorbs, while B enters a mobile precursor state and moves along the surface until it encounters A_{ad} . Then, the reaction occurs and AB can desorb. Each of these reactions can also proceed in the reverse direction.

In UHV, most surface reactions follow a LH mechanism. However, it is not sure that the LH mechanism predominates under all conditions, because it can be shown that ER and PM mechanisms are attenuated at low pressure. Thus, the mechanism depends on the reaction conditions and can change for the same reaction and surface. The ER mechanism is important especially for very reactive species B which occur for example in plasma processes employed in the production of electronic materials. LH and ER mechanisms can be distinguished by varying the pressure of one reactant while keeping that of the other constant. Then, the high-pressure limit for the rate in a LH reaction is zero, while the high-pressure limit of the non-adsorbing species B in a ER reaction approaches a constant saturation value [La87]. Precursors are difficult to detect because of their short life time. It is possible, however, to perform molecular beam experiments which can identify the PM mechanism [Ma96].

Another classification of surface reactions was given by Boudart, who distinguished between structure-sensitive and -insensitive reactions, depending on whether the rate varies strongly with the surface structure or not [Bo69]. Completely structure-insensitive reactions have not been reported, but the degree of sensitivity varies indeed from reaction to reaction. An example for an extremely structure-sensitive reaction is $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, whose rate varies by $\approx 10^{21}$ with geometry, whereas the CO oxidation belongs to the rather insensitive reactions with a variation of only 6 [Ma96]. LH reactions generally tend to be much less structure sensitive than ER and PM reactions.