9 Adsorption

9.1 Introduction

In this chapter we deal with adsorption. Adsorption is the accumulation of a substance at an interface. We first concentrate on the simplest case: Adsorption of small, uncharged molecules to the solid–gas interface. Unless the solid is in ultrahigh vacuum, gas molecules will adsorb to its surface due to attractive intermolecular forces such as the omnipresent van der Waals forces. The amount adsorbed is determined by several parameters. The most important one is the partial pressure of the molecules P. At the surface, the rotational and vibrational freedom of adsorbed molecules is usually reduced. Even their electrical properties may change. Some molecules diffuse laterally or the molecules might react on the surface; these processes are highly important in the understanding of catalysis. Finally, molecules might desorb again into the gaseous phase. Adsorption and desorption rates determine the equilibrium amount on the surface.

We extend our description to adsorption at the solid–liquid interface. For many systems we can use the same models as for gas adsorption on a solid surface, we only have to replace the pressure P by the concentration c. The adsorption of macromolecules to surfaces is briefly discussed in Section 10.3.2. For macromolecules desorption is often negligible and thermodynamic equilibrium is only reached after a very long time, if at all.

Instructive reviews about adsorption are Refs. [8,361]. A good overview on the adsorption of water to solid surfaces is Ref. [362].

9.1.1 Definitions

Let us first introduce the most important definitions. The material in the adsorbed state is called **adsorbate**. The substance to be adsorbed (before it is on the surface) is called the **adsorpt** or **adsorptive**. The substance, onto which adsorption takes place, is the **adsorbent** (Fig. 9.1).

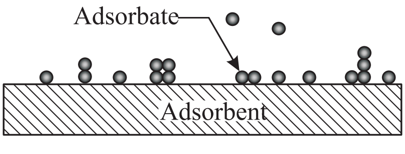

Figure 9.1: Definitions of adsorbent, adsorpt, and adsorbate.

An important question is how much of a material is adsorbed to an interface. This is described by the adsorption function $\Gamma = f(P,T)$, which is determined experimentally. It indicates the number of adsorbed moles per unit area. In general, it depends on the temperature. A graph of Γ versus P at constant temperature is called an **adsorption isotherm**. For a better understanding of adsorption and to predict the amount adsorbed, **adsorption isotherm equations** are derived. They depend on the specific theoretical model used. For some complicated models the equation might not even be an analytical expression.

All gases adsorb to solid surfaces below a critical temperature because of the van der Waals attraction. In general, when adsorption is dominated by physical interaction rather than chemical bonding, we talk about **physisorption**. Physisorption is characterized by several features:

- The sublimation energy is in the order of 20–40 kJ/mol.
- The adsorbate is still relatively free to diffuse on the surface and to rotate.
- The molecular structure of the solid does not change with physisorption except for some molecular solids (e.g. ice, paraffin, polymers).
- An adsorption equilibrium is quickly established. When lowering the pressure the gas desorbs reversibly (except in porous solids).

If the adsorption energy is of the order of chemical binding energies we talk about **chemisorption**. Characteristic properties are:

- Typical sublimation energies of 100–400 kJ/mol.
- Often there are specific binding sites. The adsorbate is relatively immobile and usually does not diffuse on the surface.
- Even on covalent or metallic solids there is often a surface reconstruction.
- Due to the strong binding, experiments in UHV are possible because the molecules practically do not desorb.

Oxidation can be viewed as the chemisorption of oxygen. For example, nickel and silicon are oxidized at ambient conditions. The resulting oxide layer is thermodynamically more stable and passivates the pure material below it. Another important example is the oxidation of aluminum which provides the metal with a very hard roughly 100 nm thick aluminum oxide (Al_2O_3) layer. To stabilize the aluminum surface even more and to passivate it against reactive chemicals the thickness of the oxide layer can be increased electrochemically. This procedure is called the eloxal process (*el*ectrolytical *ox*idation of *al*uminum).

9.1.2 The adsorption time

A useful parameter to characterize adsorption is the adsorption time. Let us first assume that no forces act between the surface and a gas molecule. Then, if a molecule hits the surface, it is reflected elastically with the same energy. An energy transfer between the surface and gas molecule does not take place. As a consequence "hot" molecules do not cool down even when they hit a cold surface. The residence time in proximity to the surface can be estimated by

$$\tau = \frac{2\Delta x}{\bar{v}_x} \approx \frac{2\Delta x}{\sqrt{k_B T/m}}, \tag{9.1}$$

where Δx is the thickness of the surface region and $\bar{v}_x$ is the mean velocity normal to the surface. Example: N_2 at 25°C, $\Delta x = 1$ Å, $\bar{v}_x \approx 300$ m/s, $\tau \approx 7 \times 10^{-13}$ s. This is in the order of typical vibration periods of 10^{-13} s.

An attractive force between the gas molecule and the surface increases the average residence time of the molecule at the surface to

$$\tau = \tau_0 \cdot e^{Q/k_B T}, \tag{9.2}$$

with $\tau_0 \approx 10^{-13}...10^{-12}$ s. Q is the heat of adsorption. To be more precise we have to identify the inverse of τ_0 with a surface bond vibration frequency. Values for various atoms and molecules adsorbed to well defined surfaces are given in Table 9.1. Heats of adsorption up to 10 kJ/mol refer to practically no adsorption and residence times are below 10 ps. $Q =$ 40 kJ/mol is characteristic for physisorption. Residence times become significantly longer and depending on the precise value of Q, can assume quite different values. Chemically adsorbed molecules ($Q \geq 100$ kJ/mol) practically do not leave the surface again.

Table 9.1: Heats of adsorption Q, surface bond vibration frequencies τ_0^{-1}, and adsorption times τ at 27°C. Results from Ref. [363].

	H/W(100)	Hg/Ni(100)	CO/Ni(111)	N_2/Ru(100)	Xe/W(111)
Q (kJ mol^{-1})	268	115	125	31	40
τ_0^{-1} (Hz)	3×10^{13}	10^{12}	8×10^{15}	10^{13}	10^{15}
τ (s)	10^{33}	10^{8}	7×10^{5}	3×10^{-8}	9×10^{-9}

Another useful parameter is the **accommodation coefficient** α. The accommodation coefficient is defined by the temperature of the molecules before the impact T_1, the surface temperature T_2, and the temperature of the reflected molecules T_3 [364]:

$$\alpha = \frac{T_3 - T_1}{T_2 - T_1} \tag{9.3}$$

For an elastic reflection, the mean velocity of the molecules before and after hitting the surface are identical and so are the temperatures: $T_1 = T_3$. Then $\alpha = 0$. If the molecules reside a long time on the surface they have the same temperature, after desorption, as the surface: $T_2 = T_3$ and $\alpha = 1$. Thus, the accommodation coefficient is a measure of how much energy is exchanged before a molecule leaves the adsorbent again.

9.1.3 Classification of adsorption isotherms

Depending on the physicochemical conditions, a great variety of adsorption isotherms are experimentally observed. Eight common examples are shown in Fig. 9.2 [7, 365].

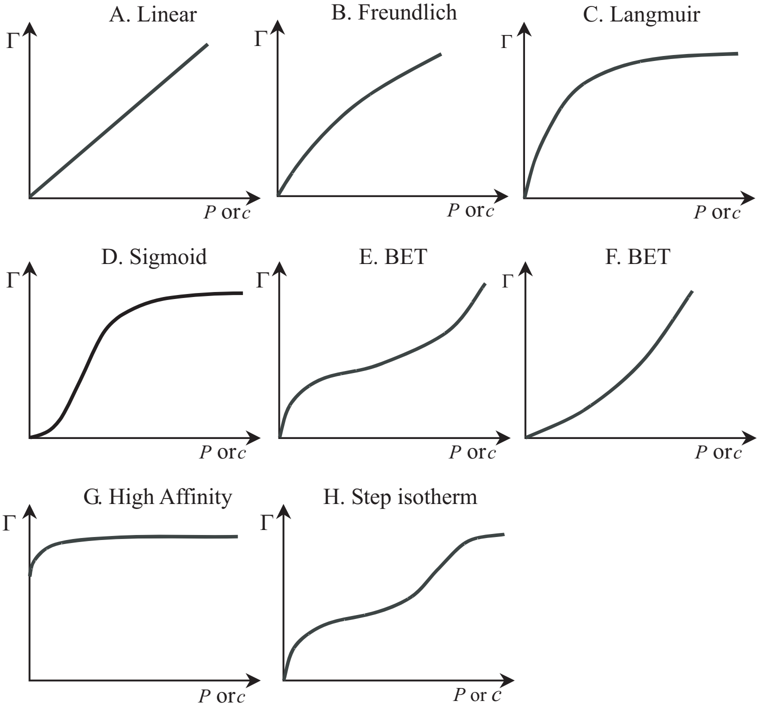

Figure 9.2: Schematic plot of eight types of adsorption isotherms commonly observed. If adsorption from the gas phase is studied, the abscissa is the partial pressure P. For adsorption from solution the concentration c is used.

The most simple type, A, is that of a linear increase. It is described by the Henry adsorption isotherm equation:

$$\Gamma = K_H P \tag{9.4}$$

K_H is a constant in units of mol m^{-2} Pa^{-1} for gases and L/m^2 for solutions. It is the ideal limiting law for low Γ.

Type B is very common. It is concave with respect to the abscissa. Most surfaces are heterogeneous. There are adsorption sites, which have a high affinity, and regions, which have a low affinity. The high affinity sites are occupied first, which accounts for the steep increase at low pressure. Another reason is sometimes a lateral repulsion between adsorbed molecules. This type of adsorption isotherm is described by the Freundlich[1] adsorption isotherm equation [366]:

$$\Gamma = K_F \cdot P^q \tag{9.5}$$

K_F and q ($q < 1$) are constants.

---

[1] Herbert Max Finlay Freundlich, 1880–1941. German physicochemist.

Type C is called the Langmuir[2] type because it can be described by the Langmuir adsorption isotherm equation:

$$\theta = \frac{K_L P}{1 + K_L P} \qquad \text{with} \qquad \theta = \frac{\Gamma}{\Gamma_{mon}} \tag{9.6}$$

Here, θ is the relative coverage and K_L is a constant, called the "Langmuir constant". Γ_{mon} is the maximum amount adsorbed which, in the case of Langmuir adsorption, is a monolayer. Type C adsorption isotherms are characterized by a saturation at high concentrations. A possible reason is that the surface is completely filled with adsorbed molecules. Langmuir adsorption is often observed for the adsorption from solution but only rarely for the adsorption of gases. This type of adsorption isotherm can also be observed for porous materials. Once all pores have been filled the isotherm saturates (see Section 9.4.3).

A sigmoidal isotherm (type D) indicates cooperative effects. A molecule binds to the surface better if it can interact with a neighboring adsorbed molecule. As a consequence of this lateral interaction two-dimensional condensation occurs. In order to observe sigmoidal isotherms, flat and homogeneous adsorbents are required.

Type E is common for the adsorption of gases. Usually the first concave part is attributed to the adsorption of a monolayer. For higher pressures more layers adsorb on top of the first one. Eventually, if the pressure reaches the saturation vapor pressure, condensation leads to macroscopically thick layers. It can be described by the BET adsorption isotherm equation Eq. (9.37) (see below).

Type F is expected if the binding of the first monolayer to an adsorbent is weaker than the binding of molecules to already adsorbed molecules. This is the case if the heat of adsorption is lower than the heat of condensation. It can also be described by the BET theory.

Type G is a high-affinity adsorption isotherm. The molecules bind so strongly that no rest can be detected in the solution or gas phase. The difference to the Langmuir type is quantitative not qualitative. It is often observed for polymer or proteins adsorbing from solution.

Step isotherms (type H) are observed with porous materials and characterized by a second inhibition. At low pressure a single layer of molecules adsorbs to the surface as for Langmuir adsorption. At intermediate pressures, multilayers start to form and the pores are filled. The saturation at high pressures is caused by the reduction of effective surface area once the pores have been filled.

9.1.4 Presentation of adsorption isotherms

An adsorption isotherm is a graph of the amount adsorbed versus the pressure of the vapor phase (or concentration in the case of adsorption from solution). The amounts adsorbed can be described by different variables. The first one is the surface excess Γ in mol/m^2. We use the Gibbs convention (interfacial excess volume $V^\sigma = 0$). For a solid surface the Gibbs dividing plane is localized directly at the solid surface. Then we can convert the number of moles adsorbed N^σ to the surface excess by

$$\Gamma = \frac{N^\sigma}{A}, \tag{9.7}$$

where A is the total surface area.

---

[2] Irving Langmuir, 1881–1957. American physicist and chemist, spent most of his time at the General Electric Company. Nobel prize for chemistry in 1932.

Adsorption is often studied using powders or porous materials because the total surface area is large even for small amounts of adsorbent. In a typical experiment the volume (V) or the mass ($m = V/\rho$) adsorbed per gram of adsorbent, is measured. Theoretical models always describe an adsorption per surface area. In order to compare theoretical isotherms to experimentally determined adsorption results, the specific surface area needs to be known. The specific surface area Σ (in m^2/kg) is the surface area per kg of adsorbent. Once the specific surface area is known, the area can be calculated by $A = m_{ad}\Sigma$, where m_{ad} is the mass of the adsorbent.

The abscissa of an adsorption isotherm plot is usually the pressure. For gases it is given in Pa. If we are studying the adsorption of a vapor in equilibrium with its liquid the relative vapor pressure P/P_0 is plotted.

9.2 Thermodynamics of adsorption

9.2.1 Heats of adsorption

Heats of adsorption are important characteristics of adsorption because they provide information regarding the driving forces for adsorption. Several heats, energies, enthalpies, and other quantities of adsorption have been defined. For a detailed discussion see Refs. [367, 368].

We first introduce the **integral molar energy of adsorption**:

$$\Delta_{ad}U_m^{int} = U_m^{\sigma} - U_m^{g} \tag{9.8}$$

It is the energy difference between N^{σ} moles of gas adsorbed U_m^{σ} (per mol) and the same amount free in the gas phase U_m^{g}. The next important quantities are the **integral molar enthalpy of adsorption**

$$\Delta_{ad}H_m^{int} = H_m^{\sigma} - H_m^{g} \tag{9.9}$$

and the **integral molar entropy of adsorption**

$$\Delta_{ad}S_m^{int} = S_m^{\sigma} - S_m^{g} \tag{9.10}$$

They are defined in complete analogy to the integral molar energy. The difference between the energy and the enthalpy of adsorption is usually small. If we treat the free gas as being ideal, the difference is $\Delta_{ad}U_m^{int} = \Delta_{ad}H_m^{int} + RT$. At 25°C RT is only 2.4 kJ/mol. For this reason we do not need to worry too much about whether a heat of adsorption is the adsorption enthalpy or the internal adsorption energy, if we only want to estimate is.

Let us now consider how these quantities are related to experimentally determined heats of adsorption. An essential factor is the condition under which the calorimetric experiment is carried out. Under constant volume conditions, $\Delta_{ad}U_m^{int}$ is equal to the total heat of adsorption. In such an experiment a gas reservoir of constant volume is connected to a constant volume adsorbent reservoir (Fig. 9.3). Both are immersed in the same calorimetric cell. The total volume remains constant and there is no volume work. The heat exchanged equals the integral molar energy times the amount of gas adsorbed:

$$Q = \Delta_{ad}U_m^{int} \cdot N^{\sigma} \tag{9.11}$$

In general, $\Delta_{ad}U_m^{int}$ is negative (otherwise the substance would not adsorb) and heat is released upon adsorption.

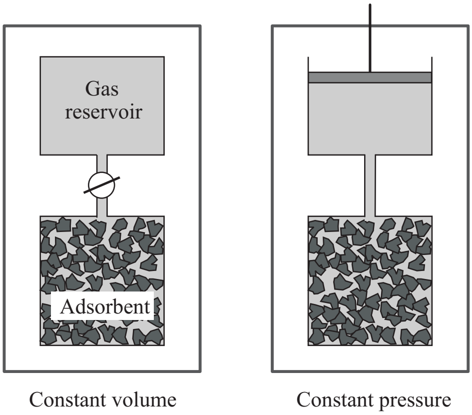

Figure 9.3: Schematic drawing of calorimeters for measuring heats of adsorption under constant volume and constant pressure conditions. The active volume is filled with the adsorbent usually in the form of a powder.

In practice, most calorimetric experiments are carried out under constant pressure. By moving the piston down, the pressure in the cell is increased and the heat release is measured. In this case the heat exchanged is equal to the integral enthalpy of adsorption :

$$Q = \Delta_{ad}H_m^{int} \cdot N^{\sigma} \tag{9.12}$$

The integral molar entropy of adsorption is obtained from a well-known thermodynamic relation: for a reversible, isothermal process the heat is equal to the change in entropy multiplied by the temperature. This directly leads to

$$\Delta_{ad}S_m^{int} = \frac{\Delta_{ad}H_m^{int}}{T} \tag{9.13}$$

One word about the Gibbs energies of adsorption. In equilibrium the molar Gibbs energy of adsorption is zero: $\Delta_{ad}G_m = \mu^{\sigma} - \mu^{g} = 0$. The reason is simple. In equilibrium and for constant P and T the chemical potential of the molecules in the gas phase μ^g is equal to the chemical potential of adsorbed molecules μ^{σ}. What is not zero is the **standard Gibbs energy of adsorption**

$$\Delta_{ad}G_m^0 = \mu^{0\sigma} - \mu^{0g} \tag{9.14}$$

It is a molar quantity but since the name is so long the "molar" is not explicitly stated. The problem with $\Delta_{ad}G_m^0$ is that we cannot measure it directly but its value depends on the specific model of adsorption used. We return to it when introducing the Langmuir model.

9.2.2 Differential quantities of adsorption and experimental results

We have introduced integral molar quantities, which indicates that there are corresponding differential quantities. Integral refers to the fact that the total amount of adsorbed gas is involved. In contrast, the **differential molar energy of adsorption** is determined only by the last infinitesimal amount adsorbed. It is defined as

$$\Delta_{ad}U_m^{dif} = \left.\frac{dU^\sigma}{dN^\sigma}\right|_{T,A} - \left.\frac{dU^g}{dN^\sigma}\right|_{T,A} \tag{9.15}$$

U^g is the total internal energy of the free gas. Since usually the amount adsorbed is small compared to the total amount of gas in the reservoir the properties of the free gas do not change significantly during adsorption. Thus, $dU^g/dN^\sigma = U_m^g$ which leads to

$$\Delta_{ad}U_m^{dif} = \left.\frac{dU^\sigma}{dN^\sigma}\right|_{T,A} - U_m^g \tag{9.16}$$

It involves the change of the internal surface energy upon adsorption of an infinitesimal amount of gas at constant temperature and total surface area.

We have to distinguish between integral and differential quantities because the energy changes with the amount adsorbed. This can have at least three causes: First, most surfaces are energetically heterogeneous and the binding sites with a high binding energy are occupied first. Second, in general the first monolayer has a different binding energy from the next layer because its adsorption is dominated by the interaction of the solid adsorbent with the gas molecule. For the second layer the interaction between adsorbed gas molecules with gas molecules is important. Third, if molecules interact laterally with neighboring molecules on the surface it is energetically more favorable for molecules to adsorb to a partially covered surface.

By analogy, the **differential molar enthalpy of adsorption** and the **differential molar entropy of adsorption** are defined as:

$$\Delta_{ad}H_m^{dif} = \left.\frac{dH^\sigma}{dN^\sigma}\right|_{T,\gamma} - H_m^g \tag{9.17}$$

$$\Delta_{ad}S_m^{dif} = \left.\frac{dS^\sigma}{dN^\sigma}\right|_{T,A} - S_m^g \tag{9.18}$$

Physical adsorption of gases on solids is virtually always enthalpically driven ($\Delta_{ad}H_m^{dif} < 0$). Entropically driven adsorption can exist but usually the entropy of molecules on a surface is much lower than in the gas phase. Vibrational, rotational, and also translational degrees of freedom are restricted on surfaces.

■ **Example 9.1.** As an example, a typical adsorption isotherm for benzene adsorbing to graphitized carbon blacks is shown in Fig. 9.4 [369]. Graphitized carbon blacks are produced by heating carbon in the absence of air to 3000°C. The initially spherical carbon particles become polyhedral with faces consisting mainly of homogeneous basal planes of single crystal graphite. In the adsorption isotherm, three regimes can be distinguished:

- At very low pressures ($P/P_0 < 0.1$) the adsorption isotherm rises steeply. Adsorbing molecules find many free binding sites. These very few molecules on the surface have a chance to bind to strong binding sites at grain boundaries. This can also be seen from the differential heats of adsorption: at coverages below 0.3 μmol/m^2 the heat of adsorption is maximal.

- Monolayer coverage is reached at a pressure of $P/P_0 \approx 0.1$. At this point the steep slope of the adsorption isotherm levels off. For the first monolayer, a roughly constant heat of adsorption of 43 kJ/mol is observed. This is about 9 kJ/mol higher than the heat of condensation of benzene.

- At higher vapor pressures $P/P_0 > 0.1$) multilayers are formed. In the multilayer region the slope becomes steeper again with increasing pressure. For $P \rightarrow P_0$ the adsorbed layer gets very thick because macroscopic condensation sets in. The differential heat of adsorption is slightly above the heat of condensation, but significantly lower than the value for the first monolayer.

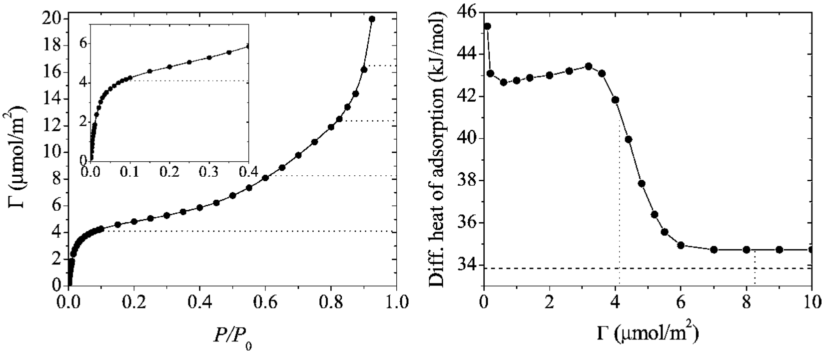

Figure 9.4: Left: Adsorption isotherm for benzene (C_6H_6) adsorbing to graphitized thermal blacks at 20°C. The insert shows the adsorption isotherm for low coverages in more detail. Dotted lines indicate mono- or multilayer coverages at multiples of 4.12 μmol/m^2. The equilibrium vapor pressure of benzene at 20°C is $P_0 = 10.2$ kPa. Right: Differential heat of adsorption versus adsorbed amount. The dashed line corresponds to the heat of condensation of bulk benzene. Redrawn after Ref. [369].

9.3 Adsorption models

9.3.1 The Langmuir adsorption isotherm

A simple model to describe adsorption was presented by Langmuir [370]. Langmuir assumed that on the surface there are a certain number of binding sites per unit area S (fig. 9.5). S is in units of mol/m^2 (or m^{-2}). Of these binding sites S_1 are occupied with adsorbate and $S_0 = S - S_1$ are vacant. The adsorption rate in moles per second and per unit area is proportional to the number of vacant binding sites S_0 and to the pressure: $k_{ad}PS_0$. The desorption rate is proportional to the number of adsorbed molecules S_1 and equal to $k_{de}S_1$, where k_{de} is a constant. In equilibrium the adsorption rate must be equal to the desorption rate; otherwise the number of adsorbed molecules would change. Therefore

$$k_{de}S_1 = k_{ad}PS_0 = k_{ad}P \cdot (S - S_1) \tag{9.19}$$

$$\Rightarrow k_{de}S_1 + k_{ad}PS_1 = k_{ad}PS \Leftrightarrow \frac{S_1}{S} = \frac{k_{ad}P}{k_{de} + k_{ad}P} \tag{9.20}$$

S_1/S is the coverage θ. With $K_L = k_{ad}/k_{de}$ we get the Langmuir equation :

$$\theta = \frac{K_L P}{1 + K_L P} \tag{9.21}$$

The Langmuir constant is given in Pa^{-1}, k_{ad} is given in $\mathrm{s}^{-1}\mathrm{Pa}^{-1}$, and k_{de} is in s^{-1}.

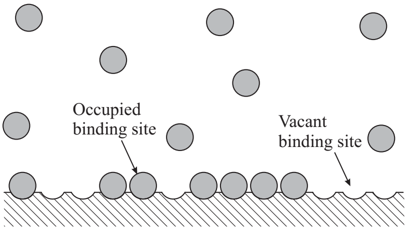

Figure 9.5: Schematic drawing of the Langmuir adsorption model.

Typical Langmuir adsorption isotherms are plotted in figure 9.6 for different values of the Langmuir constant. If adsorption from solution is considered, the pressure P has to be replaced by the concentration c and the Langmuir constant is given in units of L mol^{-1} instead of Pa^{-1}.

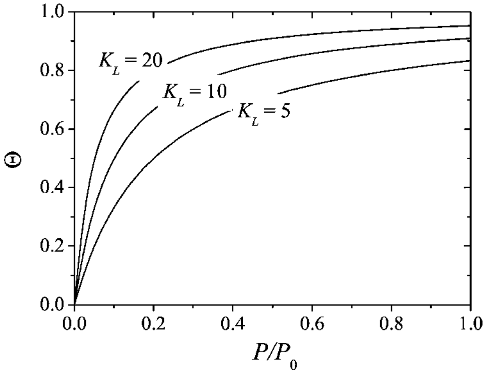

Figure 9.6: Langmuir adsorption isotherms plotted as coverage θ versus relative vapor pressure for three different Langmuir constants. The pressure and the Langmuir constants are normalized by dividing them by P_0.

Alternatively, the Langmuir adsorption isotherm equation can be expressed by the number of adsorbed moles per gram or surface area

$$\Gamma = \frac{\Gamma_{mon} K_L P}{1 + K_L P} \tag{9.22}$$

Here, Γ_{mon} is the number of adsorbed moles per gram or per unit area of substrate, when all binding sites are occupied and a monolayer of molecules is bound. Γ_{mon} is related to the surface area occupied by one adsorbed molecule σ_A by $\Gamma_{mon} = \Sigma / (N_0 \sigma_A)$ or $\Gamma_{mon} = 1/(N_0\sigma_A)$.

What is the significance of the constants k_{ad} and k_{de}? k_{de} is the inverse of the adsorption time:

$$k_{de} = \frac{1}{\tau_0} \cdot e^{-Q/k_BT} \tag{9.23}$$

In order to calculate k_{ad} we remember the kinetic theory of ideal gases and Eq. (2.1) of example 2.1. Equation (2.1) tells us how many gas molecules of mass m hit a certain area A per second. If we take the area to be the active area of one binding site σ_A the number of molecules hitting one binding site per second is

$$\frac{\sigma_A P}{\sqrt{2\pi m k_B T}} \tag{9.24}$$

If we assume that each molecule that hits the surface sticks to it, expression (9.24) is equal to $k_{ad}P$ and we get

$$k_{ad} = \frac{\sigma_A}{\sqrt{2\pi m k_B T}} \tag{9.25}$$

For the Langmuir constant we obtain

$$K_L = K_L^0 \cdot e^{Q/k_BT} \qquad \text{with} \qquad K_L^0 = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} \tag{9.26}$$

■ **Example 9.2.** Let us estimate the Langmuir constant for the physisorption of a gas to a solid surface at a temperature of 120 K. We take τ_0 to be 10^{-13} s, use a typical molecular cross-section of 10 Å^2, and assume a heat of adsorption of 20 kJ/mol. As a gas we consider nitrogen ($M = 0.028$ kg/mol). It is more convenient to use Eq. (9.26) in molar rather than molecular units:

$$K_L = K_L^0 \cdot e^{Q/RT} \qquad \text{with} \qquad K_L^0 = \frac{N_A \sigma_A \tau_0}{\sqrt{2\pi MRT}} \tag{9.27}$$

Inserting the values leads to $K_L^0 = 4.55 \times 10^{-10}$ Pa^{-1} and $K_L = 0.23$ Pa^{-1}.

Please keep in mind, that the calculated adsorption rate is an upper limit. It can also be used for the calculation of the condensation rate of a liquid. We define a **condensation coefficient** or **sticking probability** as the ratio between the actual condensation and the (just calculated) upper limit. The sticking probability can be determined from molecular beam experiments. Examples: For N_2 on tungsten the sticking probability at 27°C is 0.61 [372]. For H_2O on ice at 200 K it is close to one [371]. The sticking probability can also be significantly below 1. Then the Langmuir constant is reduced accordingly.

The kinetic derivation has the disadvantage that it refers to a certain model. The Langmuir adsorption isotherm, however, applies under more general conditions and it is possible to derive it with the help of statistical thermodynamics [8,373]. Necessary and sufficient conditions for the validity of the Langmuir equation (9.21) are:

- The molecules bind to well-determined binding sites on the adsorbent.
- Each binding site can bind only one molecule.
- The binding energy is independent of the presence of other bound molecules.

9.3.2 The Langmuir constant and the Gibbs energy of adsorption

The Gibbs energy of adsorption depends on the specific model used (Section 9.2.1). Here, we demonstrate this with the Langmuir model and derive a relation between the standard Gibbs energy of adsorption $\Delta_{ad}G_m^0$ and the Langmuir constant. Therefore, we treat the binding and desorption of gas molecules to surface binding sites, like a chemical reaction. Chemical equilibria are commonly characterized by an equilibrium constant K. For the dissociation reaction AB $\rightleftharpoons$ A + B this constant is given by

$$K = \frac{[A] \cdot [B]}{[AB]} \tag{9.28}$$

It is related to the standard Gibbs energy of the reaction $\Delta_r G_m^0$ by

$$\Delta_r G_m^0 = -RT \cdot \ln K \tag{9.29}$$

Here, $[AB]$, $[A]$, and $[B]$ are the concentrations (for gas reactions, the pressures) of the bound (educt) and dissociated molecules (products), respectively.

Let us apply this formalism to the adsorption of gas molecules to a surface. The adsorption equilibrium constant in units of Pa is

$$K_{ad} = \frac{S_0 P}{S_1} \tag{9.30}$$

It is related to the standard Gibbs energy of adsorption by

$$\Delta_{ad} G_m^0 = -RT \cdot \ln K_{ad} \tag{9.31}$$

Inserting $S - S_1 = S_0$ leads to

$$K_{ad} = \frac{(S - S_1)\, P}{S_1} \Rightarrow S_1 = \frac{SP}{K_{ad} + P} \tag{9.32}$$

Since $\theta = S_1/S$ we immediately get

$$\theta = \frac{P}{K_{ad} + P} \qquad \text{with} \qquad K_{ad} = \exp\left(-\frac{\Delta_{ad} G_m^0}{RT}\right) \tag{9.33}$$

Comparison with Eq. (9.21) shows that

$$K_L = \frac{1}{K_{ad}} \tag{9.34}$$

When inserting real numbers in Eqs. (9.31) and (9.33) it is important to remember that pressures are given in units of normal pressure, that is 10^5 Pa.

9.3.3 Langmuir adsorption with lateral interactions

One assumption of the Langmuir model is that the adsorbed molecules do not interact with each other. It is possible to modify the theory and take such an interaction into account. Therefore we assume that each binding site has n neighboring binding sites. The average number of neighbors of an adsorbed molecule is $n\theta$. When we denote the additional binding energy related to the interaction between a pair of neighboring molecules by E_P, we can consider lateral interactions by modifying the Langmuir equation. Therefore it is convenient to write the Langmuir equation as

$$\frac{\theta}{1-\theta} = K_L' P$$

and modify the Langmuir constant:

$$K_L' = K_L^0 \cdot \exp\left(\frac{Q + nE_P\theta}{RT}\right) = K_L \cdot \exp\left(\frac{nE_P\theta}{RT}\right) \qquad (9.35)$$

This equation is sometimes called the Frumkin–Fowler–Guggenheim (FFG) isotherm [374–376]. For $\beta \equiv nE_P/RT < 4$ lateral interactions cause a steeper increase of the adsorption isotherm in the intermediate pressure range. Characteristic of all Langmuir isotherms is a saturation at high partial pressures $P/P_0 \to 1$.

A remarkable shape is calculated with Eq. (9.35) for $\beta > 4$. A region is obtained where the θ-versus-P curve has a negative slope (dotted curve in Fig. 9.7). This is physically nonsense: The coverage is supposed to decrease with increasing pressure and for one pressure there are three possible values of θ. In reality this is a region of two-phase equilibrium. Single adsorbed molecules and clusters of adsorbed molecules coexist on the surface. The situation is reminiscent of the three-dimensional van der Waals equation of state which can be used to describe condensation.

As an example, Fig. 9.7 shows adsorption isotherms of krypton on the (0001) face of graphite. The dashed lines were fitted using Eq. (9.35) with $\beta = 4.5$. In reality the coverage increases steeply and the two-phase region can be identified. Figure 9.7 shows another typical feature of adsorption: The amount adsorbed decreases with increasing temperature.

9.3.4 The BET adsorption isotherm

In Langmuir model, the maximal adsorption is that of a monolayer. Langmuir adsorption isotherms all saturate at high vapor pressures. This is unrealistic for many cases. In order to consider the adsorption of multilayers, Brunauer, Emmett, and Teller extended the Langmuir theory and derived the so-called BET adsorption isotherm [378]. The basic idea in the BET theory was to assume a Langmuir adsorption for each of the layers (Fig. 9.8).

It is assumed that the adsorption heat for the first layer Q_1 has a particular value. For all further layers, the heat of adsorption Q_i corresponds to the heat of condensation of the liquid. Another condition is that desorption and adsorption take place only directly between vapor and surface. Adsorbed molecules are not allowed to move from one layer directly to another. In equilibrium, the desorption rate for each layer must be equal to the adsorption rate. We

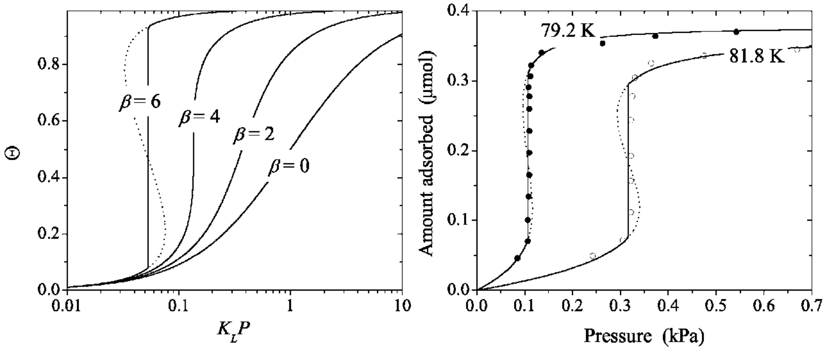

Figure 9.7: Left: Frumkin–Fowler–Guggenheim (FFG) adsorption isotherms (coverage θ versus the pressure in units of K_L^{-1}). The curves were calculated using Eq. (9.35) with $\beta = 0, 2, 4, 6$. For $\beta = 6$ the physically correct adsorption curve is plotted as a continuous curve while the one calculated with Eq. (9.35) is plotted as a dotted curve. Right: Adsorption isotherms for krypton adsorbing to the (0001) plane of graphite at two different temperatures. The dotted curves were fitted using Eq. (9.35) with $\beta = 4.5$. Experimental results were taken from Ref. [377].

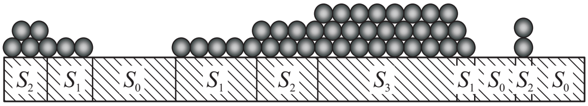

Figure 9.8: BET model of adsorption.

have the following adsorption and desorption rates:

$$\begin{array}{lll} \text{Adsorption to vacant surface sites} & k_{ad}^1 P S_0 & \\ \text{Desorption from first layer} & & = a_1 S_1 e^{-Q_1/RT} \\ \text{Adsorption to the } i^{th} \text{ layer} & k_{ad}^i P S_{i-1} & \\ \text{Desorption from the } i^{th} \text{ layer} & & = a_i S_i e^{-Q_i/RT} \end{array} \tag{9.36}$$

Here, a_1 and a_i are frequency factors like $1/\tau_0$. As a result we get

$$\frac{n}{n_{mon}} = \frac{C}{\left(1 - \frac{P}{P_0}\right) \cdot \left[1 + \frac{P}{P_0} \cdot (C-1)\right]} \cdot \frac{P}{P_0} \tag{9.37}$$

Here, n is the total number of moles adsorbed per unit area, n_{mon} is the number of adsorbed moles in one full monolayer per unit area (each binding site is occupied exactly once), P_0 is the equilibrium vapor pressure, and

$$C = \frac{a_i k_{ad}^1}{a_1 k_{ad}^i} \cdot e^{(Q_1 - Q_i)/RT} \approx e^{(Q_1 - Q_i)/RT} \tag{9.38}$$

Equation (9.37) shows that, n/n_{mon} becomes infinite for $P/P_0 \to 1$. This is what we expect because condensation sets in. For the second part of Eq. (9.38) see exercises.

Since the BET adsorption isotherm is so widely used, we describe a simple derivation [1]. It is convenient to define two parameters, α and β, according to

$$\alpha = \frac{k_{ad}^1 P}{a_1}\, e^{Q_1/RT} \qquad \text{and} \qquad \beta = \frac{k_{ad}^i P}{a_i}\, e^{Q_i/RT} \tag{9.39}$$

Using these parameters we can write

$$S_1 = \alpha S_0 \qquad \text{and} \qquad S_2 = \beta S_1 \tag{9.40}$$

and in general

$$S_i = \beta^{i-1} S_1 = \alpha \beta^{i-1} S_0 = C \beta^i S_0 \tag{9.41}$$

The number of moles adsorbed per unit area is given by

$$n = S_1 + 2S_2 + 3S_3 + \ldots = \sum_{i=1}^{\infty} i S_i = C S_0 \sum_{i=1}^{\infty} i \beta^i = \frac{C S_0 \beta}{(1-\beta)^2} \tag{9.42}$$

Monolayer coverage can be written as

$$n_{mon} = S_0 + S_1 + S_2 + S_3 + \ldots = S_0 + C S_0 \sum_{i=1}^{\infty} \beta^i = S_0 + \frac{C S_0 \beta}{1-\beta} \tag{9.43}$$

Now we divide Eq. (9.42) by Eq. (9.43)

$$\frac{n}{n_{mon}} = \frac{C S_0 \beta / (1-\beta)^2}{S_0 + C S_0 \beta / (1-\beta)} = \frac{C\beta}{(1-\beta)\left[1 - \beta + C\beta\right]} \tag{9.44}$$

An essential step is to realize that the factor β is equal to P/P_0. To see this let us consider the adsorption of a vapor to its own liquid at equilibrium and hence at P_0. We take this situation to be similar to the situation of the vapor adsorbing to the ith (not the first) layer. Taking the rate of binding equal to the rate of desorption we write

$$k_{ad}^i P_0 S = a_i S e^{-Q_i/RT} \tag{9.45}$$

On both sides we insert the total number of binding sites per unit area S because all sites can serve as binding and desorption sites. This immediately leads to

$$P_0 = \frac{a_i}{k_{ad}^i}\, e^{-Q_i/RT} \tag{9.46}$$

By inserting this into Eq. (9.39) we get $\beta = P/P_0$ and with Eq. (9.44) obtain the BET isotherm equation (9.37).

Figure 9.9 shows how BET isotherms depend on the parameter C. For high values of C the binding of vapor molecules directly to the surface, is strong compared to the intermolecular interaction. Therefore, at least for low pressures, a Langmuir type of adsorption is obtained. Only at high pressures do the molecules start to form multilayers. For low values of C the molecules prefer binding to themselves while the binding energy to the surface is low. Therefore, the first monolayer only forms at relatively high pressures. Once it has formed it is easier for the next molecules to adsorb.

BET isotherms are widely used to fit experimental adsorption isotherms. Two examples, the adsorption of water to alumina and silica, are shown in Fig. 9.9 on the right. The adsorption of alumina can be fitted with the BET equation up to a relative pressure of 0.4, which is quite typical. For silica the fit is acceptable even up to $P/P_0 = 0.8$.

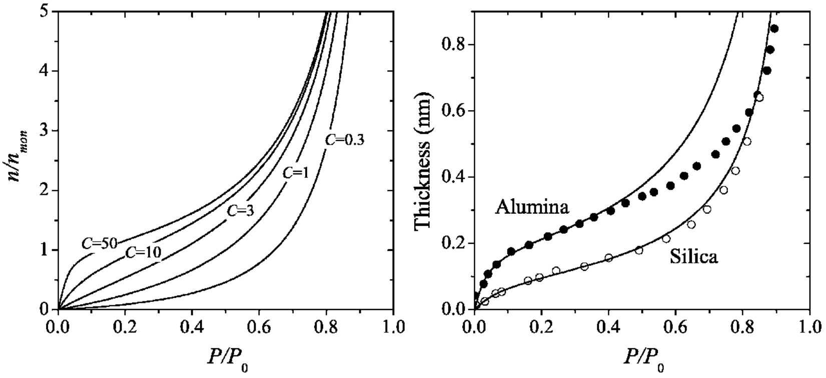

Figure 9.9: Left: BET adsorption isotherms plotted as total number of moles adsorbed, n, divided by the number of moles in a complete monolayer, n_{mon}, versus the partial pressure, P, divided by the equilibrium vapor pressure, P_0. Isotherms were calculated for different values of the parameter C. Right: Adsorption isotherms of water on a sample of alumina (Baikowski CR 1) and silica (Aerosil 200) at 20°C ($P_0 = 2.7$ kPa, redrawn from Ref. [379]). The BET curves were plotted using Eq. (9.37) with $C = 28$ (alumina) and $C = 11$ (silica). To convert from n/n_{mon} to thickness, the factors 0.194 nm and 0.104 nm were used, which correspond to $n_{mon} = 6.5$ and 3.6 water molecules per nm^2, respectively.

9.3.5 Adsorption on heterogeneous surfaces

Surfaces are usually not perfectly homogeneous. Different crystal faces are exposed, defects and other deviations from the perfect lattice are present. Often there are different types of molecules as in steel (e.g. Fe, C, Ni, Co) or in glass (e.g. SiO_2, B, Na, K) and their concentrations on the surface might vary locally.

On heterogeneous surfaces the binding energy of an adsorbate will generally not be a fixed value, but there is a distribution of binding energies. The probability of finding a binding site in the energy interval $Q \ldots Q + dQ$ is described by a distribution function $f(Q)dQ$. The experimentally observed adsorption is the sum of all adsorption events on all different kinds of binding sites. At a fixed temperature the coverage is

$$\theta(P) = \int_0^\infty \theta^H(Q,P) \cdot f(Q) \cdot dQ \qquad (9.47)$$

The distribution function is normalized:

$$\int_0^\infty f(Q)dQ = 1 \tag{9.48}$$

For the adsorption isotherm on a well determined homogeneous part of the surface $\theta^H(Q,P)$ the Langmuir equation is often used.

A relatively well-known adsorption isotherm, the Freundlich isotherm [366]

$$\theta = \left(\frac{P}{P_0}\right)^{\frac{k_BT}{2Q^*}}, \tag{9.49}$$

is obtained with an exponentially decaying distribution of adsorption sites according to $f(Q) \propto e^{-Q/Q^*}$ and assuming a Langmuir behavior for θ^H [380]. Here, Q^* is a constant which characterizes the distribution of adsorption energies. A requirement in the derivation is that $Q^* > k_BT$. This, however, is not a severe restriction because for $Q^* < k_BT$ adsorption is negligible.

Often one would like to conclude something about the distribution of the binding energies using a measured adsorption isotherm. This is difficult. Usually certain assumptions concerning θ^H have to be made [381].

9.3.6 The potential theory of Polanyi

Polanyi[3] approached the phenomenon of adsorption in a completely different way. He assumes that the molecules close to the surface feel a potential — similar to the gravitation field of the earth. One cause for this potential is the van der Waals attraction. The potential compresses the gas close to the surface, isothermally. Once the pressure becomes higher than the equilibrium vapor pressure, it condenses. In equilibrium, the chemical potential of the gas at a distance x from the surface $\mu(x, P_x)$ must be equal to the chemical potential $\mu(\infty, P)$ at a large distance away form the surface. P_x is the local pressure at a distance x, P is the partial pressure far from the surface. The differential of the chemical potential is

$$d\mu = -S_m dT + V_m dP_x + dU_m \tag{9.50}$$

S_m is the molar entropy, V_m the molar volume of the gas at a distance x, and U_m is the molar internal energy. Integrating the left side from infinite distance to a distance x leads to

$$\int_{\mu(\infty,P)}^{\mu(x,P_x)} d\mu = \mu(x,P_x) - \mu(\infty,P) = 0 \tag{9.51}$$

The integration is simple since the chemical potential is a state function. The integral is zero because in equilibrium the chemical potential should be the same everywhere. Integration of the right side of Eq. (9.50) at constant temperature leads to

$$\int_P^{P_x} V_m dP' + U_m(x) - U_m(\infty) = 0 \Rightarrow -U_m(x) = \int_P^{P_x} V_m dP' \tag{9.52}$$

---

[3] Michael Polanyi, 1891–1976. Hungarian physicist who worked in Berlin and Manchester. His son, John Charles Polanyi, received the Noble Price in chemistry in 1986.

The internal energy at $x = \infty$ was set to zero: $U_m(\infty) = 0$. Now we assume that the gas behaves like an ideal gas until it condenses. For an ideal gas we can use $V_m P' = RT$ and solve the integral:

$$-U_m(x) = RT \cdot \ln \frac{P_x}{P}. \tag{9.53}$$

To take a possible condensation of the gas into account we assume that the gas becomes liquid once the pressure exceeds the equilibrium vapor pressure P_0. The amount adsorbed is just the thickness of the liquid film multiplied by its density. The film thickness x_f is related to the number of adsorbed moles per unit area by $\Gamma = x_f / V_m^L$, where V_m^L is the molar volume of the liquid. The energy at which the pressure P_0 is reached is

$$U_m(x_f) = -RT \cdot \ln \frac{P_0}{P} \tag{9.54}$$

As an example we consider an ideal gas, which is attracted towards a surface by van der Waals interactions. In Eq. (6.13) we calculated the Gibbs free energy for the van der Waals interaction of a single molecule with a flat surface. The internal energy is a factor of two higher. Using $C \equiv \pi \rho_B C_{AB}/3$ as a constant we obtain

$$-U_m(x_f) = \frac{C}{(D_0 + x_f)^3} = RT \cdot \ln \frac{P_0}{P} \Rightarrow x_f = \sqrt[3]{\frac{C}{RT \cdot \ln(P_0/P)}} - D_0 \tag{9.55}$$

D_0 is a distance, which corresponds to the molecular radius. The number of moles adsorbed per unit area is

$$\Gamma = \frac{x_f}{V_m^L} = \frac{1}{V_m^L} \cdot \sqrt[3]{\frac{C}{RT \cdot \ln(P_0/P)}} - \frac{D_0}{V_m^L} \tag{9.56}$$

■ **Example 9.3.** Plot the estimated adsorption isotherm for water vapor on silicon oxide at 20°C. First we need to estimate the constant C. From Chapter 6 we know that it is related to the Hamaker constant A_H (Eq. 6.16): $C \equiv \pi \rho_B C_{AB}/3 = A_H / 3\pi\rho_A$. Here, ρ_A and ρ_B are the number densities of molecules in liquid water and silicon oxide, respectively. The Hamaker constant for water interacting with silicon oxide across air is $A_H = 10^{-20}$ J (Table 6.3). With a density of water of 1000 kg/m^3, a molecular weight of 18 g/mol, and a molecular radius of $D_0 \approx 1$ Å we get $V_m^L = 0.018\,\mathrm{kg mol^{-1}}/(1000\,\mathrm{kg m^{-3}}) = 18 \times 10^{-6}\,\mathrm{m^3 mol^{-1}}$ and

$$C = \frac{A_H}{3\pi\rho_A} = \frac{10^{-20}\,\mathrm{J}}{3\pi \cdot 1000\,\mathrm{kgm^{-3}}/0.018\,\mathrm{kgmol^{-1}}} = 1.9 \times 10^{-26}\,\frac{\mathrm{Jm^3}}{\mathrm{mol}}$$

$$\begin{aligned} \Gamma &= \frac{1}{V_m^L} \cdot \sqrt[3]{\frac{C}{RT \cdot \ln(P_0/P)}} - \frac{D_0}{V_m^L} \\ &= 1.1 \times 10^{-5}\,\frac{\mathrm{mol}}{\mathrm{m^2}} \cdot \sqrt[3]{\frac{1}{\ln(P_0/P)}} - 0.55 \times 10^{-5}\,\frac{\mathrm{mol}}{\mathrm{m^2}} \end{aligned} \tag{9.57}$$

Figure 9.10 shows the calculated adsorption isotherm and compares it to experimental results. The Polanyi theory predicts the general shape of the adsorption isotherm reasonably well considering that it is not a fit but a real calculation. Real adsorption is, however, stronger, which indicates that in addition to van der Waals forces other attractive forces are important.

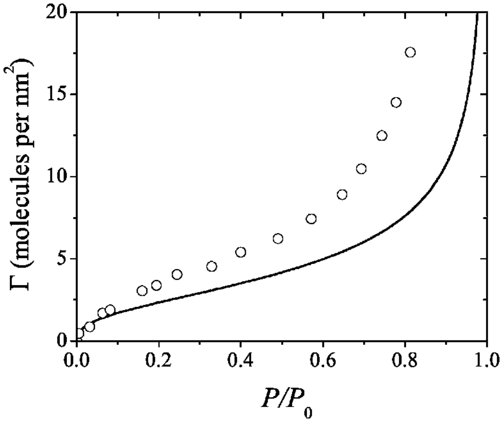

Figure 9.10: Adsorbed amount of water on a silicon oxide surfaces versus relative vapor pressure at 20°C. The continuous line was calculated with the theory of Polanyi and assuming van der Waals forces only (Eq. 9.57). Experimental results as measured on Aerosil 200 were adapted from Ref. [379] (see also Fig. 9.9). The deviation at high pressure is partially due to the porosity of the adsorbent. The equilibrium vapor pressure is $P_0 = 3.17$ kPa.

Which theory is suitable for a certain application? The adsorption theory of Henry is applicable at low pressure. This, however, is natural since it can be viewed as the first term in a series of the adsorption function. A widely used adsorption isotherm equation is the BET equation. It usually fits experimental results for $0.05 < P/P_0 < 0.35$. For very small pressures the fit is not perfect due to the heterogeneity. For higher pressures the potential theory is more suitable at least for flat, homogeneous adsorbents. It often applies to P/P_0 values from 0.1 to 0.8. Practically for $P/P_0 > 0.35$ adsorption is often dominated by the porosity of the material. A more detailed description of adsorption is obtained by computer simulations [382].

9.4 Experimental aspects of adsorption from the gas phase

9.4.1 Measurement of adsorption isotherms

Several experimental methods are applied to measure adsorption isotherms . The main problem is to determine the amount adsorbed. One method is a **gravimetric measurement**. In a gravimetric measurement the weight increase as a function of the pressure is determined. The adsorbent, usually in the form of a powder, is placed into a bulb and kept at the desired temperature. The bulb is mounted on a sensitive balance. Before the experiment, the bulb is evacuated. Then the gas of interest is admitted into the bulb at a certain pressure. The increase in weight is measured. Dividing by the total surface area of the adsorbent, we get the amount of adsorbed gas. The pressure is increased and the weight measurement is repeated. In this way a whole isotherm is recorded.

In **volumetric measurements** the volume of an adsorbed gas at constant pressure and temperature is determined. Therefore, we first determine the “dead space” or volume of the bulb by admitting some nonadsorbing (or weakly adsorbing) gas such as Helium. Then, after evacuating the bulb, the gas of interest is admitted into the bulb. This is done at constant pressure and temperature. The volume admitted into the bulb minus the dead space is the amount adsorbed.

More recently methods have also been developed to measure the adsorbed amount on single surfaces and not onto powders. Adsorption to isolated surfaces can, for instance, be measured with a **quartz crystal microbalance** (QCM) [383]. The quartz crystal microbalance consists of a thin quartz crystal that is plated with electrodes on the top and bottom (Fig. 9.11). Since quartz is a piezoelectric material, the crystal can be deformed by an external voltage. By applying an AC voltage across the electrodes, the crystal can be excited to oscillate in a transverse shear mode at its resonance frequency. This resonance frequency is highly sensitive to the total oscillating mass. For an adsorption measurement, the surface is mounted on such a quartz crystal microbalance. Upon adsorption, the mass increases, which lowers the resonance frequency. This reduction of the resonance frequency is measured and the mass increase is calculated [384–387].

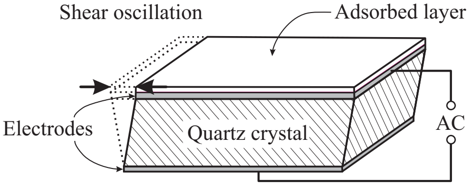

Figure 9.11: Working principle of a quartz crystal microbalance.

Another technique applicable to single flat surfaces is **ellipsometry**. To understand ellipsometry we first have to remember that the reflection of light from a surface depends on the direction of polarization. Light polarized parallel and perpendicular to the surface is reflected differently. Amplitude and phase change in a different way depending on polarization. In ellipsometry we direct a monochromatic and polarized light beam, usually that of a laser, onto a surface at a certain angle. The angle of incidence must be small enough so that the light is totally reflected. At the interface the polarization changes. Two parameters, sometimes called the ellipsometric angles Δ and Ψ, are measured. The first parameter is $\Delta = \delta_{in} - \delta_{out}$, where δ_{in} is the phase difference between the parallel and perpendicular component of the incoming wave and δ_{out} is the phase difference between the parallel and perpendicular component of the outgoing wave. The second parameter is given by $\tan\Psi = |R_p| / |R_s|$, where R_p and R_s are the reflection coefficients for the parallel and perpendicular polarized light. From the amplitude ratios and the phase shift between the incident and reflected light, we can determine the thickness of a thin film, assuming that the refractive index of the material is known.

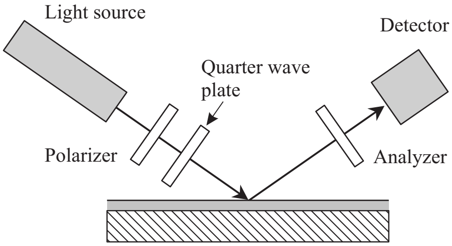

Figure 9.12: One type of ellipsometer, called a Null instrument. Polarizer and analyzer are rotated alternately until the null is found.

Different experimental configurations are used to determine the Δ and Ψ. A practical introduction into ellipsometry is Ref. [388]. One common type is the Null ellipsometer also called PCSA configuration for "polarizer–compensator–sample–analyzert't' (Fig. 9.12). In a Null ellipsometer elliptically polarized light produced by a laser, polarizer, and a quarter wave plate (or a compensator) is directed onto the surface. The polarization is adjusted by the polarizer in such a way, that perfectly linear polarized light is reflected from the sample. For linear polarized light the intensity can be decreased to zero by the analyzer. From the orientations of polarizer and analyzer at zero intensity (for given fixed properties of the compensator and angle of incidence) the ellipsometric angles can be calculated. As one example the adsotprion isotherm for nitrogen to the basal plane of graphite is shown in Fig. 9.13.

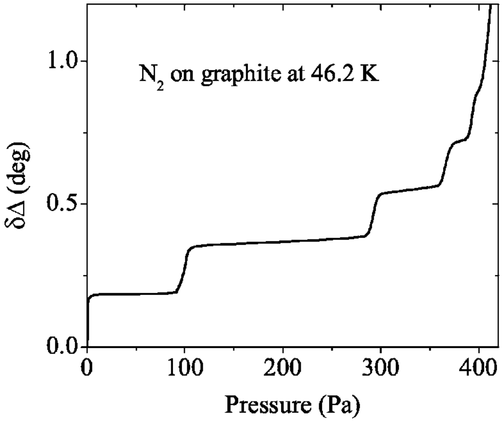

Figure 9.13: Adsorption of nitrogen to a single basal plane of graphite at a temperature of 46.2 K as determined by ellipsometry. Plotted is the change in the ellipsometric angle $\triangle$ versus pressure. The subsequent adsorption of at least four layers at defined pressures can clearly be distinguished. Redrawn from Ref. [389].

9.4.2 Procedures to measure the specific surface area

For all experiments with porous materials or powders we need to know the specific surface area. This is also important for many industrial applications and determination of the specific surface area has become a standard technique in chemical engineering of powders.

Usually specific surface areas are determined from adsorption experiments. To illustrate this let us assume that adsorption of a specific sample is adequately described by the Langmuir Eq. (9.22). From fitting experimental results we obtain Γ_{mon} in units of mol/g. Then we assume a reasonable value for the cross-section area of a gas molecule σ_A, and obtain the specific surface from $\sum = \Gamma_{mon}\sigma_A N_A$. In most practical applications the BET adsorption isotherm is used instead of the Langmuir Eq. (9.22) because it fits better. From a fit with the BET isotherm we get Γ_{mon} or n_{mon}. Some cross-sectional areas for suitable gases in Å^2 are: N_2: 16.2; O_2: 14.1; Ar: 13.8; n-C_4H_{10}: 18.1.

Table 9.2: Calculated specific surface areas Σ in m^2/g for a batch of anatas, porous glass, a silica gel, and a special sample of the protein albumin [390].

	N_2	Ar	O_2	CO	CH_4	CO_2	C_2H_2	NH_3
Anatas, TiO_2	13.8	11.6		14.3		9.6		
Porous glass	232	217				164	159	207
Silica gel	560	477	464	550		455		
Albumin	11.9	10.5	9.9		10.3			

How do we practically determine the specific surface area? We measure the adsorption isotherm of a defined mass of adsorbent and fit it with the BET equation. Usually the BET model describes adsorption for $0.05 < P/P_0 < 0.35$ reasonably well, and we can restrict the measurement to that pressure range. Most commonly the volumetric technique is applied. As a result of our measurements, we get the volume of gas adsorbed, V^{ad}. To be meaningful the conditions (pressure, temperature) at which the volume of the gas is reported, have to be given. Usually standard conditions are chosen although the actual experiment is often done at lower temperature. For the analysis we have to transform the BET adsorption equation. First, we express the number of moles adsorbed by the volumes: $n/n_{mon} = V^{ad}/V^{ad}_{mon}$, where V^{ad}_{mon} is the volume of gas required to get one complete monolayer. Inserting into Eq. (9.37) and rearrangement of leads to

$$\frac{P/P_0}{V^{ad}\left(1 - P/P_0\right)} = \frac{1}{CV^{ad}_{mon}} + \frac{P/P_0 \cdot (C-1)}{CV^{ad}_{mon}} \tag{9.58}$$

As a result we plot $\frac{P/P_0}{V^{ad}(1-P/P_0)}$ versus P/P_0. This should give a straight line with a slope $(C-1)/\left(CV^{ad}_{mon}\right)$ and an intersection with the ordinate at $1/\left(CV^{ad}_{mon}\right)$. From the slope and intersection C and V^{ad}_{mon} can be determined.

Porous materials are often analyzed with a **mercury porosimeter**. With a mercury porosimeter we can measure the pore distribution of a solid. Thus, we can determine the specific surface area. Mercury is used because of its high surface tension (0.48 N/m) it does not wet solid surfaces; typical contact angles are 140° on glass and 149° on paraffin. In the mercury porosimeter mercury is pressed with a pressure P into the pores of a solid. Only pores whose radius is larger than

$$r > \frac{2\gamma_{Hg} \cdot |\cos\Theta|}{P} \tag{9.59}$$

are filled. We measure the filled volume versus the applied pressure. To get the wetted surface area A we take the volume work and equate it with the work necessary to wet the surface:

$$PdV = -\left(\gamma_S - \gamma_{SL}\right) \cdot dA = -\gamma_{Hg} \cdot \cos\Theta \cdot dA \tag{9.60}$$

The pore is modelled as a capillary. Please note: γ_{SL} is larger in this case than γ_S and $\cos\Theta < 0$. Integration results in the entire surface area being wetted by mercury:

$$A = -\frac{1}{\gamma_{Hg} \cdot \cos\Theta} \cdot \int\limits_0^{P_{\max}} PdV \tag{9.61}$$

The method is limited to pore radii larger than ≈ 2 nm due to the maximal applicable pressure. An assumption made in the analysis is that a pore is accessible only by capillaries with larger radius. Pores with a narrow entrance and a wide body (called “ink bottle pores”) lead to a hysteresis in the volume–pressure curve.

9.4.3 Adsorption on porous solids — hysteresis

Until now we have mainly treated adsorption onto non-porous surfaces. In reality, most industrial and many natural materials are porous: Textiles, paper, bricks, sand, porous rocks, food products, zeolites etc. We start our discussion with a classification of pores according to their size, which is recommended by IUPAC:

- Macropores have a diameter larger than 50 nm. Macropores are so wide that gases adsorb virtually to flat surfaces.
- Mesopores are in the range of 2–50 nm. Capillary condensation often dominates the filling of mesopores. Below the critical temperature, multilayers arise. Pores, on one hand, limit the number of layers, but on the other hand, capillary condensation can occur.
- Micropores are smaller than 2 nm. In micropores the structure of the adsorbed fluid is significantly different from its macroscopic bulk structure. Confined liquids are a highly active area of research because of their unique properties. An important example of a microporous materials are zeolites, which are used for catalysis.

This classification is certainly not perfect because the filling of pores is also determined by their shape (cylinders, slits, cones, irregular) and pores may be separate or connected.

To characterize the size of pores, the hydraulic radius a_h was introduced. The hydraulic radius is the ratio of void volume and void area. For a long cylindrical pore of length l and radius r $(r \ll l)$ the hydraulic radius is for instance

$$a_h = \frac{\pi r^2 l}{2\pi r l} = \frac{r}{2} \tag{9.62}$$

Above a certain critical temperature no multilayers should adsorb. Hence, even porous solids should behave like flat surfaces, if no pores of molecular size are present. Capillary condensation plays a role only below the critical temperature.

Adsorption to porous materials is often characterized by hysteresis in the adsorption behavior. Such a hysteresis is observed when, after the adsorption process, a desorption experiment is done in which the pressure is progressively reduced from its maximum value and the desorption isotherm is measured. During the desorption process, the liquid phase vaporizes from the pores. The desorption isotherm does not precisely track the adsorption isotherm, but lies above it. Moreover isotherms often flatten out with high P/P_0 values, because filling up of pores decreases the available surface area.

It is widely accepted that two mechanisms contribute to the observed hysteresis. The first mechanism is thermodynamic in origin [391,392]. It is illustrated in Fig. 9.14 for a cylindrical pore of radius r_c. The adsorption cycle starts at a low pressure. A thin layer of vapor condenses onto the walls of the pore (1). With increasing pressure the thickness of the layer increases. This leads to a reduced radius of curvature for the liquid cylinder a. Once a critical radius a_c is reached (2), capillary condensation sets in and the whole pore fills with liquid (3). When decreasing the pressure again, at some point the liquid evaporates. This point corresponds to a radius a_m which is larger than a_c. Accordingly, the pressure is lower. For a detailed discussion see Ref. [393].

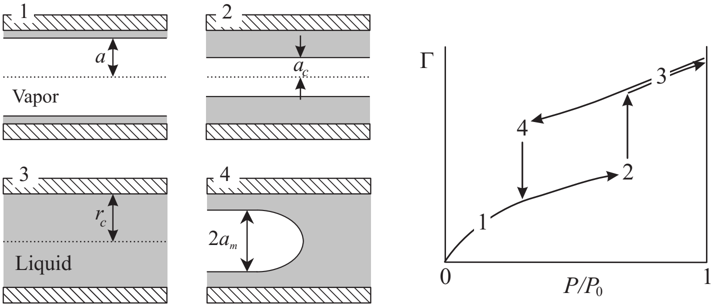

Figure 9.14: Filling and emptying of a cylindrical solid pore with liquid from its vapor and the the corresponding schematic adsorption/desorption isotherms.

In the second mechanism the topology of the pore network plays a role [394]. During the desorption process, vaporization can occur only from pores that have access to the vapor phase, and not from pores that are surrounded by other liquid-filled pores. There is a "pore blocking" effect in which a metastable liquid phase is preserved below the condensation pressure until vaporization occurs in a neighboring pore. Therefore, the relative pressure at which vaporization occurs depends on the size of the pore, the connectivity of the network, and the state of neighboring pores. For a single "ink bottle" pore this is illustrated in Fig. 9.15. The adsorption process is dominated by the radius of the large inner cavity while the desorption process is limited by the smaller neck.

In recent years the understanding of the adsorption of vapors has significantly progressed. This is mainly due to the fact that more materials with defined pore sizes can be made [395,

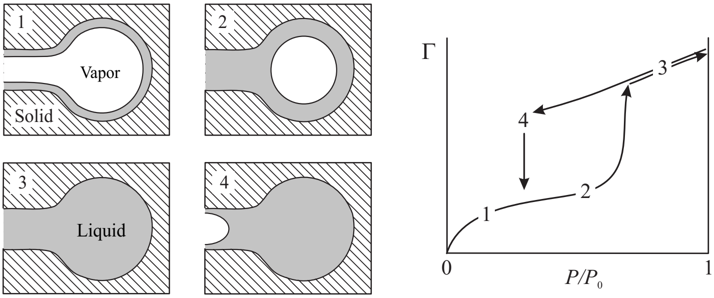

Figure 9.15: Filling and emptying of a solid ink bottle pore with liquid from its vapor and the corresponding adsorption/desorption isotherms.

396]. An example of the adsorption to one such material is shown in Fig. 9.16. The siliceous material, called MCM-41, contains cylindrical pores [397]. With increasing pressure first a layer is adsorbed to the surface. Up until a pressure of $P/P_0 \approx 0.45$ is reached, this could be described by a BET adsorption isotherm equation. Then capillary condensation sets in. At a pressure of $P/P_0 \approx 0.75$, all pores are filled. This leads to a very much reduced accessible surface and practically to saturation. When reducing the pressure the pores remain filled until the pressure is reduced to $P/P_0 \approx 0.6$. The hysteresis between adsorption and desorption is obvious. At $P/P_0 \approx 0.45$ all pores are empty and are only coated with roughly a monolayer. Adsorption and desorption isotherms are indistinguishable again below $P/P_0 \approx 0.45$.

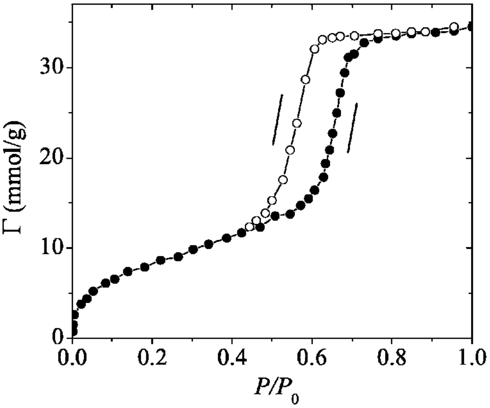

Figure 9.16: Adsorption isotherms of Argon at 87 K in siliceous material MCM-41 with cylindrical pores of 6.5 nm diameter. Redrawn after Ref. [398].

9.4.4 Special aspects of chemisorption

Chemisorption is usually connected with a chemical reaction. Therefore, it is not surprising that the molecules must overcome an activation energy E_A (Fig. 9.17). Often the molecules first physisorb to the surface and in a second, much slower, step the bond is established. For desorption both the adsorption energy Q and the activation energy must be overcome. The desorption energy E_{des} is thus larger than the adsorption energy .

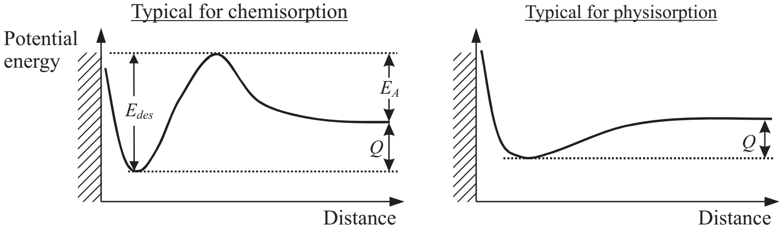

Figure 9.17: Potential energy profile versus distance for chemisorption and physisorption.

Experimentally, information about the adsorption and desorption rates is obtained with the help of programmed desorption. One procedure is flash desorption: A surface is instantaneously heated up (normally in vacuum) and we measure the temporal desorption of material, for instance with a mass spectrometer. Heating is usually done with a laser pulse (PLID, pulsed laser induced thermal desorption).

Another possibility is to heat the surface up slowly and to measure the quantity of desorbed material versus the temperature. This is called temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS). Usually distinct maximums are observed which correspond to the breaking of specific bonds.

For the simple case of a first-order desorption process we briefly describe the analysis; a first order desorption is described by $d\theta/dt = -k_{de}\theta$. Desorption is assumed to be an activated process. The desorption rate, that is the decrease in coverage or the number of molecules coming off the surface per unit time, is

$$k_{de}^* = -\frac{d\theta}{dt} = a\theta \cdot e^{-E_{des}/RT} \tag{9.63}$$

Here, $a \approx 10^{-13}\mathrm{s}^{-1}$ is a frequency factor. In the experiment we increase the temperature of the surface linearly with a rate β (in K s^{-1}): $T = T_0 + \beta t$. A desorption maximum occurs at a temperature T_m. At this maximum we have $dk_{de}^*/dt = 0$. Differentiation of Eq. (9.63) leads to

$$\begin{aligned} \frac{dk_{de}^*}{dt} &= a \cdot \frac{d\theta}{dt} \cdot e^{-E_{des}/RT_m} + a\theta \cdot e^{-E_{des}/RT_m} \cdot \frac{E_{des}\beta}{RT_m^2} = 0 \\ \Rightarrow & \quad a \cdot e^{-E_{des}/RT_m} = \frac{E_{des}\beta}{RT_m^2} \end{aligned} \tag{9.64}$$

Thus, the desorption energy can be calculated from T_m and a. An example, the desorption of thiols from gold, is described in Ref. [402].

9.5 Adsorption from solution

In this section we consider the adsorption of molecules to surfaces in liquids. Adsorption from solution is a diverse subject. Here, we can only introduce some basic, general features.

A more comprehensive introduction is Ref. [399]. We restrict ourselves to uncharged species and dilute solutions (not binary mixtures). The important subject of polymer adsorption is described in Ref. [400]. Adsorption of surfactants is discussed in Ref. [401]. Adsorption of ions and formation of surface charges was treated in Chapter 5. In dilute solutions there is no problem in positioning the Gibbs dividing plane, and the analytical surface access is equal to the thermodynamic one, as occurs in the Gibbs equation. For a thorough introduction into this important field of interface science see Ref. [8].

Some basic concepts developed for vapor adsorption can also be applied to the adsorption from solution. However, there are also differences. In solution, adsorption is always an exchange process. It is an exchange process in two ways: First, a molecule adsorbing to a surface has to replace solvent molecules. Second, the adsorbing molecule gives up part of its solvent environment. This has several practical consequences:

- Molecules do not only adsorb because they are attracted by the surfaces but because the solution might reject them. An example of this is hydrophobic substances in water. They readily adsorb to many surfaces because of their dislike for water, rather than a strong interaction with the adsorbent.

- A thermodynamic treatment has to take into account the exchange character of adsorption. If one adsorbing molecule replaces ν solvent molecules at the surface, the whole reaction is

  $$A^L + \nu S^\sigma \rightleftharpoons A^\sigma + \nu S^L \tag{9.65}$$

  Here, A^L is the adsorpt in solution, A^σ is the adsorbate at the surface, S^L represents a solvent molecule surrounded by other solvent molecules, while S^σ is a solvent molecule at the surface.

- Multilayer formation is less common in solutions than in the gas phase because the interaction with the adsorbent is screened by the solvent and the adsorbing molecules have alternative partners.

As an example of adsorption from solution Fig. 9.18 shows the isotherm of n-docosane ($C_{22}H_{46}$) and n-$C_{28}H_{58}$ adsorbing to graphite in n-heptane (C_7H_{16}). The longer-chain alkanes are strongly preferred to heptane, indicating that they adsorb in a flat position. A sigmoidal shape is observed with $C_{22}H_{46}$, a hint that the molecules also interact laterally with neighbors. For $C_{28}H_{58}$, adsorption is so strong that even trace amounts all adsorb to the surface. This strong adsorption leads to a high affinity adsorption isotherm (type G in Fig. 9.2). The conclusions — parallel orientation and cooperativity between the adsorbed molecules — are supported by structural studies with the STM.

9.6 Summary

- Adsorption isotherms show the amount of a substance adsorbed versus the partial pressure or the concentration.

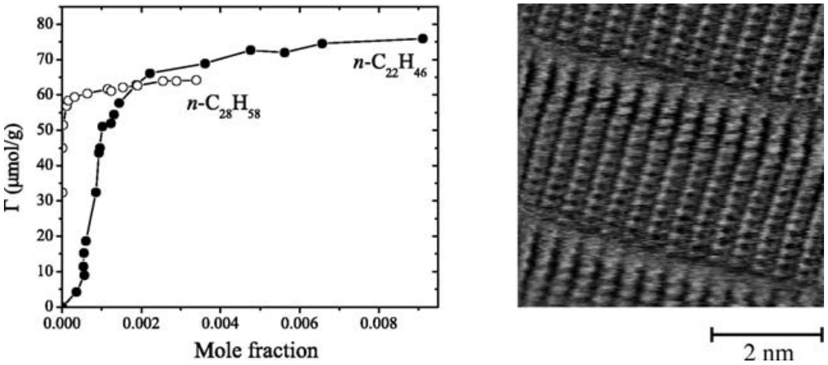

Figure 9.18: Left: Adsorption isotherms of long-chain n-alkanes from n-heptane to graphite (Vulcan 3G). Redrawn from Ref. [403]. Right: Scanning tunneling microscope image of heptacosane ($C_{27}H_{56}$) adsorbed to the basal plane of graphite form an organic solution. The alkanes lay flat on the graphite surface and are highly oriented. Images were kindly provided by J. Rabe [404].

- Physisorption is characterized by a relatively weak binding with adsorption energies of a few 10 kJ/mol. In chemisorption a chemical bond is established between the adsorbate and the adsorbent; desorption energies are in the range of 100–400 kJ/mol.

- To describe adsorption, Langmuir assumed that independent binding sites exist on the adsorbent. This leads to the adsorption equation

$$\theta = \frac{K_L P}{1 + K_L P}$$

  The adsorption isotherm saturates at high partial pressure and the maximal amount adsorbed is that of a monolayer.

- Usually adsorption is more realistically described by the BET model. BET theory accounts for multilayer adsorption. The adsorption isotherm goes to infinity at relative partial pressures close to one, which corresponds to condensation.

- Experimentally, adsorption isotherms are determined by gravimetric or volumetric measurements for powders or porous adsorbents. For isolated flat surface a quartz microbalance or an ellipsometer can be applied to measure adsorption isotherms.

- For porous adsorbents capillary condensation is a common phenomenon. It leads to hysteresis in the adsorption curve.

- In liquids, adsorption is an exchange process in which adsorbed molecules replace liquid molecules.

9.7 Exercises

1. Discuss the significance of the Langmuir constant K_L. Therefore discuss how the Langmuir isotherm increases for low pressures. At which pressure is the adsorbent half covered?

2. Estimate the Langmuir parameter K_L for nitrogen at 79 K assuming $\sigma_A = 16$ Å^2, $\tau_0 = 10^{-12}$ s, $M = 28$ g/mol and $Q = 2$ kcal/mol.

3. BET adsorption isotherm: Verify that $\frac{a_i k_{ad}^1}{a_1 k_{ad}^i} \cdot e^{(Q_1 - Q_\nu)/RT} \approx e^{(Q_1 - Q_\nu)/RT}$ in Eq. (9.38).

4. What is the hydraulic radius for a powder of close-packed spherical particles of radius R? 74% of the volume is filled by the particles.

5. Kern and Findenegg measured the adsorption of n-docosane ($C_{22}H_{46}$) in heptane solution to graphite [403]. They used a porous graphite with a specific surface area of 68 m^{2}g^{-1} as determined from BET adsorption isotherms with N_2. Γ_{max}, which is assumed to correspond to monolayer coverage, is found to be 88.9 μmol/g. Can you conclude something about the structure of the adsorbed molecules? What is the area occupied by one molecule compared to its size?

6. Behm et al. studied the adsorption of CO to Pd(100) [323]. Therefore they did a series of TDS experiments at a coverage of $\theta = 0.15$. Using the following heating rates β they observed a desorption peak at

β (Ks^{-1})	0.5	1.2	2.5	4.9	8.6	15.4	25
T_m (K)	449	457	465	473	483	489	492

   Calculate the desorption energy E_{des} and the frequency factor a assuming first-order kinetics. Therefore rewrite Eq. (9.64) so that on one side you have $\ln\left(T_m^2/\beta\right)$.