

Statistical Thermodynamic Models of Adsorption

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Contents

1	Introduction and terminology	1
2	Lennard-Jones model	2
3	A simple model	3
3.1	A grand canonical examination	3
3.2	Thermodynamical properties	4
4	A more advanced model	5
4.1	Grand canonical approach	5
4.2	Thermodynamical properties of our advanced model	5
5	Adsorption and dissociation of molecules	6
6	Langmuir's adsorption isotherms	6
7	Example: Adsorption of Oxygen	7
8	Lattice gas models	7
9	Discussion	8

Abstract

Gaseous molecules or atoms which are in contact to a solid surface are often attracted to it. They can even get bound to the surface. Such a phenomenon is called adsorption. This short review will show how such a system can be described in statistical thermodynamics. Especially the grand canonical way will be emphasized for how treating simple models. As a result we find Langmuir's isotherm and some thermodynamical properties of adsorbed layers.

1 Introduction and terminology

Adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on a solid or liquid surface. The molecules or atoms that bind to the surface are called the **adsorbate** or, especially when the adsorbate consists of atoms, it is called **adatom**. The process itself is called **adsorption**. Removal of the molecules from the surface is called **desorption**. The **substrate** is simply the solid surface onto which adsorption can occur. The substrate is also occasionally (although not here) referred to as the adsorbent. With **coverage** one means the extent of adsorption of

a species onto a surface. Usually coverage is denoted by the lower case Greek θ .

A qualitative distinction is usually made between **chemisorption** and **physisorption**, in terms of the relative binding strengths and mechanisms. In chemisorption, a strong chemical bond is formed between the adsorbate atom or molecule and the substrate. Energies of a few $eV/atom$ are typical of chemisorption.

Physisorption is weaker, and is often described as implying that no chemical interaction is present. This can't really be true, because if there were no attractive interaction, then the atom wouldn't stay on the surface for any measurable time - it would simply bounce back into the vapor. A better distinction is that in physisorption, the energy of interaction is largely due to the van der Waals force. Typical systems are rare gases on layer compounds and other similar systems. Physisorption energies are of order $50 - 500 meV/atom$. These energies are comparable to the sublimation energy of a rare gas solid.

On a more fundamental level, when a molecule is chemisorbed, the electrons are shared between the adsorbate and the surface. As a result, the adsorbate's electronic structure is significantly perturbed. The surface's electronic structure is perturbed to a lesser extent. In contrast, physisorption is governed by polarization (i.e. van der Waals) force. The surface does not share electrons with the adsorbate. As a result, the electronic structure of the adsorbate is perturbed to a much lesser extent.

Adsorption of molecules often proceeds in two stages. A first precursor stage, has all the characteristics of physisorption, but this state is metastable. In this state the molecule may re-evaporate, or it may stay on the surface long enough to transform irreversibly into a chemisorbed state - the second stage. This transition is rather dramatic, usually resulting in splitting the molecule and adsorbing the individual atoms: **dissociative chemisorption**. See chapter 2 for further details. The adsorption energies for the precursor phase are similar to physisorption of rare gases, but may contain additional contributions from the dipole, quadrupole, etc. moments of the molecules.

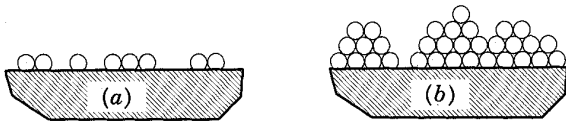


Figure 1: An illustration of (a) monolayer adsorption and (b) multilayer adsorption

The dissociation stage can be explosive - literally. The heat of adsorption is given off suddenly, and can be imparted to the resulting adatoms. As an example bulk solid F_2 is however quite dangerous, and has an alarming tendency to blow up by reacting dissociatively with its container.

Note that there is a distinction between **adsorption**, where a gas binds directly to the surface of a solid, and **absorption**, where the gas dissolves directly into the bulk of a fluid.

Usually scientists distinguish also between **multilayer adsorption**, where several layers of adsorbate partly cover the substrate, and **monolayer adsorption** where all the adsorbate is held in close proximity to the solid. Both types of adsorption are illustrated in 1. Chemisorption is limited to one monolayer where as physisorption is able to form multilayer.

The adsorption of molecules onto a surface is a necessary requirement to any surface chemical processes. For example, in the case of a surface catalyzed reaction it is possible to subdivide the whole continuously cycling process into the following five basic steps:

1. Diffusion of reactants to the active surface
2. Adsorption of one or more reactants onto the surface
3. Surface reaction
4. Desorption of products from the surface
5. Diffusion of products away from the surface

The above scheme does not only emphasize the importance of the adsorption process but also its reverse - namely desorption.

In chapter 2 the Lennard-Jone's model is described which differentiates between dissociative and nondissociative adsorption. The description is only qualitative. In chapter 3 some calculations are done with the simplest model. We will treat this with a grand canonical partition function and get as a result the entropy for this model and further some thermodynamical properties. In the following chapter 4 the same calculations

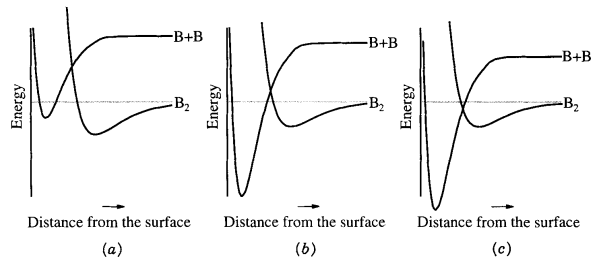


Figure 2: Lennard-Jones's model of (a) pure molecular adsorption, (b) activated dissociative adsorption, (c) unactivated dissociative adsorption

are done but with molecules with internal degrees of freedom. The next step is a model which adsorption and dissociation in chapter 5. Despite of the thermodynamical properties the main result of each model is the Langmuir isotherm which will be discussed in chapter 6. A biochemical example will be given in chapter 7, which is not much appropriate for this review but is very interesting for us, because experimental data are fitted very well with a Langmuir isotherm. In Chapter 8 a short description, mainly the ansatz, for a lattice gas model is given. It should only emphasize the connection to an Ising model. In the last chapter 9 one will find a small selection of modern research areas which are based on adsorption.

2 Lennard-Jones model

Langmuir [7] found that it was convenient to distinguish between two different types of adsorption: **nondissociative adsorption** when the adsorbing molecules stay intact during adsorption, and **dissociative adsorption** processes, where bonds break when molecules adsorb. Nondissociative adsorption processes are sometimes called **monomolecular adsorption** processes.

In 1932 Lennard-Jones proposed a simple model to try to put the distinction between monomolecular and dissociative adsorption on a more fundamental basis. Consider the interaction of a B_2 molecule with a flat surface. One can imagine that as the molecule approaches the surface, the molecule interacts via a Lennard-Jones potential. Following Lennard-Jones it is assumed that the interaction energy is a function of distance only.

Note that in the gas phase it takes some energy, $E_d^{B_2}$, to dissociate the B_2 molecule. As a result, at long distances from the surface the energy of two separate B atoms will be $E_d^{B_2}$ times higher than the energy of a B_2 molecule. Now when the two B atoms interact with the surface, they can form bonds. As a result, the energy of the two separate B atoms will be lowered. As one can see in figure 2 the energy of the molecular state and the

dissociated state cross at some point above the surface.

Lennard-Jones extended these ideas to three cases shown in figure 2 because molecular and dissociative adsorption is associated with the height of the crossing point between these two states.

The first case is one where the molecular state is more strongly bound than the dissociated state. In that case molecular adsorption is the preferred bonding configuration.

The second case is one where the dissociative state has a lower energy than the nondissociated state, but there is a finite activation barrier to get into the dissociative state. An incoming molecule could dissociate in this case, but if the activation barrier is high, one would still see mainly molecular adsorption.

In the third case the barrier lies below a dissociated depression and an activation barrier between them but below the energy of the B_2 molecule. As a result, an incoming B_2 molecule will always have enough energy to surmount the barrier and dissociate. Dissociative adsorption should be the norm in this situation.

Note that it is possible for the incoming molecule to lose some of its energy before the molecule dissociates. In that case, the molecule can get caught in the molecular depression and has to surmount a barrier to dissociate. In such a case, the molecular state is called a **molecular precursor**. For a more complex behavior see [9] p. 120.

3 A simple model

3.1 A grand canonical examination

Over the years, there have been many attempts to understand the geometry of adsorbed layers. Key early work was done by Langmuir 1918 [7], who showed that he could model the adsorption process by assuming that the adsorbate was held on a series of distinct sites on a solid surface, as illustrated in 3. It took many years before people began to realize that multiple sites are important even during adsorption on single crystals. As in picture 4 one can see that the so-called on-top or **linear site** lies directly above a surface atom, and a **bridge-bound site** between two adjacent surface atoms. Subsequent investigators have also suggested that CO on $Pt(111)$ can adsorb on **triply coordinated site** above a three-fold hollow. In this review we only want to treat the simple linear site adsorption.

Let us suppose a box of volume V which contains an ideal monatomic gas with no spin. The gas is in contact to a surface with N sites. Each site can hold only one atom which represents a state with energy $-\varepsilon_0$. The positive ε_0 is also called the bond energy. A similar model where a site can hold up to two molecules is given in [2] on p. 388.

In our system the particle number of adsorbed atoms is not constant. The surface exchanges atoms with the surrounding gas which can therefore be treated as a particle and energy reservoir. After long enough time the system reaches thermodynamical equilibrium at temperature T and the chemical potential μ . We are able to calculate the characteristics of such a system when we know the grand canonical partition function Z_G . Because the atoms are not distinguishable the partition function can be divided to factors for each site, which are all the same and therefore

$$Z_G = \xi^N \quad . \quad (1)$$

One site can contain either zero or one single atom. So ξ becomes:

$$\xi = 1 + e^{\beta(\varepsilon_0 + \mu)}, \quad \text{with } \beta = \frac{1}{kT} \quad . \quad (2)$$

With equation (2) and (1) one can derive the average number of adsorbed atoms:

$$N_a = kT \frac{\partial \ln Z_G}{\partial \mu} = N \frac{e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}} \quad (3)$$

The ratio

$$\theta := \frac{N_a}{N} = \frac{1}{1 + e^{-\beta(\varepsilon_0 + \mu)}} \quad (4)$$

defines the coverage of adsorbed atoms to the surface or the probability of an occupied site and is therefore called adsorption rate. Note that equation (4) is similar to the Fermi-Dirac distribution function.

The total energy E_a of adsorbed particles can be calculated with

$$E_a - \mu N_a = - \frac{\partial \ln Z_G}{\partial \beta} \quad , \quad (5)$$

and one obtains that

$$E_a = \frac{-\varepsilon_0 N}{1 + e^{-\beta(\varepsilon_0 + \mu)}} = -\varepsilon_0 N_a \quad , \quad (6)$$

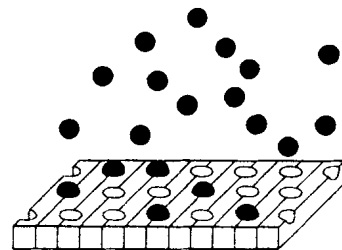


Figure 3: Langmuir's model of the adsorption of gases on surfaces. The white holes represent possible adsorption sites, while the black dots represent adsorbed or free molecules

which is plausible and we could have imagined because every adsorbed particle holds only one possible energy $-\varepsilon_0$. Finally we calculate the entropy S_a directly from the grand canonical partition function with the help of the grand canonical potential A which is defined as

$$A := -kT \ln Z_G = E_a - \mu N_a - TS_a \quad . \quad (7)$$

Therefore

$$S_a = kN \ln \left(1 + e^{\beta(\varepsilon_0 + \mu)} \right) - \frac{\varepsilon_0 + \mu}{T} N_a \quad . \quad (8)$$

Entropy S_a can also be written as a function of adsorbed atoms N_a and the total number of particles

$$S_a = k [N \ln N - N_a \ln N_a - (N - N_a) \ln (N - N_a)] \quad . \quad (9)$$

Equation (9) can also be obtained by supposing equivalent sites, the particles on each site do not interact, and all of the adsorbed atoms are immobile, then one can show [10] p. 212 that the number of possibilities of placing N_a particles on N sites is

$$\Omega_a = \frac{N!}{(N - N_a)! N_a!} \quad . \quad (10)$$

With $S_a = k \ln \Omega_a$ and Stirling's formula $\ln(N!) \approx N \ln N - N$ we derive equation (9).

3.2 Thermodynamical properties

If one knows the temperature T and the chemical potential μ of a special system, it is possible to calculate the thermodynamical properties. In our system with monatomic ideal gas μ , T and pressure p are connected through [3], p. 411

$$e^{\beta\mu} = \frac{p}{kT} \left(\frac{2\pi\hbar^2}{mkT} \right)^{\frac{3}{2}} \quad . \quad (11)$$

Replacing μ by equation (11) we obtain the properties of our system as a function of parameters T and p which are measurable.

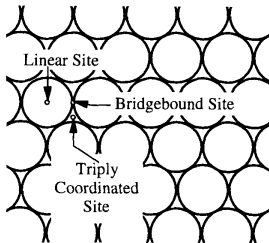


Figure 4: Illustration of linear, bridgebound, and triply coordinated sites

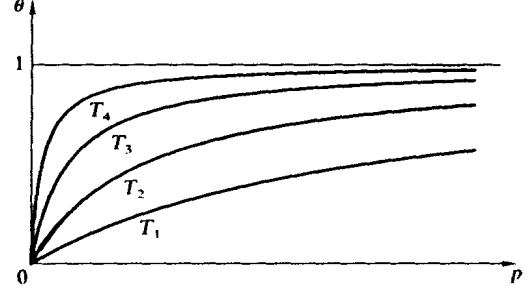


Figure 5: A plot of some typical Langmuir isotherms: the surface coverage or rate of adsorption as a function of pressure p for different temperatures $T_1 > T_2 > T_3 > T_4$

It is convenient to define

$$p_0(T) := kT \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{-\beta\varepsilon_0} \quad . \quad (12)$$

Inserting (11) and (12) in the definition of coverage (equation 4) the rate of adsorption can be written as

$$\theta := \frac{N_a}{N} = \frac{p}{p + p_0(T)} \quad (13)$$

which is one of Langmuir's key result [7]. Further description of this result will be presented in chapter 6. See also figure 5.

The average energy E_T of the total system, which consists of the gas and the adsorbate, is the sum of the energy of the adsorbed atoms E_a and the free gaseous atoms E_g . Because of our assumptions every free atom has the energy $\frac{3}{2}kT$. With N_G as their average number we get

$$E_T = E_g + E_a = \frac{3}{2} N_g kT - \varepsilon_0 N_a \quad . \quad (14)$$

To calculate the heat capacity of the whole system we use the conservation law of particles: $N_g + N_a = \text{const}$. So the heat capacity can be written as

$$C_V := \frac{dE_T}{dT} = \frac{3}{2} N_g k + \left(\frac{3}{2} kT + \varepsilon_0 \right) \left(\frac{dN_g}{dT} \right)_{eq} \quad . \quad (15)$$

Let us denote Δn as the fluctuating atoms which get adsorbed to the surface and therefore ΔE_T as the change of energy of the whole system, then the adsorption heat at constant volume Q_V is defined as the ratio of those two values

$$Q_V := \frac{\Delta E_T}{\Delta n} \quad . \quad (16)$$

Since $\Delta E_T < 0$ if $\Delta n > 0$, the adsorption heat is negative. This means that heat will be released during the

adsorption process. In our simple model with equation (14) rewritten as $\Delta E_T = (-\varepsilon_0 - \frac{3}{2}kT) \Delta n$ we obtain

$$Q_V = - \left(\varepsilon_0 + \frac{3}{2}kT \right) . \quad (17)$$

4 A more advanced model

4.1 Grand canonical approach

The previous simple model can easily be converted to a more advanced model. Let us suppose an ideal gas again but this time consisting of molecules with internal degrees of freedom (i.e. rotation, vibration, spin,...). The surface contains N sites with a series of possible energies ε_λ for one site. Each site can hold only one molecule or none and therefore the grand canonical partition function has the form

$$\xi = 1 + \sum_{\lambda} e^{-\beta(\varepsilon_\lambda - \mu)}, \quad Z_G = \xi^N . \quad (18)$$

Defining the sum $z_a(\beta) := \sum_{\lambda} e^{-\beta\varepsilon_\lambda}$ as the canonical partition function for an adsorbed molecule we get for the average number of adsorbed particles similar to equation (3) in the previous section

$$N_a = N \frac{z_a(\beta)e^{\beta\mu}}{1 + z_a(\beta)e^{\beta\mu}} , \quad (19)$$

for coverage

$$\theta := \frac{N_a}{N} = \frac{z_a(\beta)}{z_a(\beta) + e^{-\beta\mu}} , \quad (20)$$

and for the average energy of adsorbed particles

$$E_a = \mu N_a - \frac{\partial \ln Z_G}{\partial \beta} = -N \frac{\frac{dz_a}{d\beta} e^{\beta\mu}}{1 + z_a(\beta)e^{\beta\mu}} . \quad (21)$$

The entropy can further be written as

$$S_a = k [N \ln N - N_a \ln N_a - (N - N_a) \ln (N - N_a)] + N_a k \frac{d}{dT} (T \ln z_a(\beta)) , \quad (22)$$

which implies the entropy for each molecule on a certain site plus the entropy of configuration like in equation (9).

4.2 Thermodynamical properties of our advanced model

Like in the previous section 3 we want to express our formulas in dependence of measurable values like T , and p . In [3] on p. 455 we find the following connection

$$e^{\beta\mu} := \frac{p}{kT} \frac{V}{z_g} = \frac{p}{kT} \left(\frac{2\pi\hbar^2}{mkT} \right)^{\frac{3}{2}} \frac{1}{\zeta(T)} \quad (23)$$

in which $\zeta(T)$ represents the internal partition function of a molecule. It contains rotational, vibrational and spin degrees of freedom, and it depends only on temperature T . The function z_g is the canonical partition function of a gaseous molecule.

Similar to (12) we define

$$p_0(T) := \frac{kT}{V} \frac{z_g}{z_a} = kT \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \frac{\zeta(T)}{z_a(\beta)} , \quad (24)$$

and we find again Langmuir's important correlation:

$$\theta := \frac{N_a}{N} = \frac{p}{p + p_0(T)} \quad (25)$$

We have found the same result in the previous chapter in equation (13).

Each free molecule has an average energy of

$$\bar{\varepsilon}_g = - \frac{\partial \ln z_g(\beta)}{\partial \beta} = \frac{3}{2}kT - \frac{\partial \ln \zeta}{\partial \beta} . \quad (26)$$

N_g denotes the average number of free molecules and therefore we find for the total system $E_T = \bar{\varepsilon}_g N_g + \bar{\varepsilon}_a N_a$ and for the heat capacity

$$C_V := \frac{dE_T}{dT} = \frac{d\bar{\varepsilon}_g}{dT} N_g + \frac{d\bar{\varepsilon}_a}{dT} N_a + (\bar{\varepsilon}_g - \bar{\varepsilon}_a) \left(\frac{dN_g}{dT} \right)_{eq} . \quad (27)$$

We see that the heat capacity is a sum of the heat capacity of the gaseous molecules, the adsorbed molecules and a correction term. This additional term considers that some particles will evaporate during a heating process.

Equation (27) can also be converted to a function of T and p .

$$C_V = C_V^{(g)} + C^{(a)} + kT \left[T \left(\frac{\partial \ln p}{\partial T} \right)_{N_a} - 1 \right] \left(\frac{dN_g}{dT} \right)_{eq} \quad (28)$$

with $C_V^{(g)} = N_g \frac{d\bar{\varepsilon}_g}{dT}$ as the heat capacity of gaseous molecules and $C^{(a)} = N_a \frac{d\bar{\varepsilon}_a}{dT}$ as the heat capacity of adsorbed particles. If one knows the isotherms of Langmuir, it is possible to calculate $C^{(a)}$ with a measurement of C_V .

5 Adsorption and dissociation of molecules

It is possible that molecules dissociate during the adsorption process. Each atom then occupies a different site. In this review we treat, for simplicity, the adsorption and dissociation of a diatomic molecule of identical atoms. Explicitly we will do some calculation with H_2 .

The essential difference between the previous sections is that we have to handle with two different chemical potentials now, because our gas consists of molecules and the monolayer of atoms. We finally find through some canonical considerations [3] p. 946, for the chemical equilibrium

$$\mu_{H_2} = 2\mu_H \quad . \quad (29)$$

The coverage is equal to the previous section

$$\theta := \frac{N_a}{N} = \frac{z_a(\beta)}{z_a(\beta) + e^{-\beta\mu_H}} \quad . \quad (30)$$

The chemical potential of H_2 relates to p through

$$e^{\beta\mu_{H_2}} = \frac{p}{kT} \left(\frac{2\pi\hbar^2}{m_{H_2}kT} \right)^{\frac{3}{2}} \frac{1}{\zeta_{H_2}(T)} \quad , \quad (31)$$

and therefore we find for Langmuir's isotherm as a function of p

$$\theta = \frac{\sqrt{p}}{\sqrt{p} + \sqrt{\tilde{p}_0(T)}} \quad (32)$$

with

$$\tilde{p}_0 := kT \left(\frac{m_{H_2}kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \frac{\zeta_{H_2}(T)}{z_a(T)^2} \quad . \quad (33)$$

The main difference between here and the previous examples is the behavior with \sqrt{p} for low $p \ll \tilde{p}_0$.

6 Langmuir's adsorption isotherms

The so-called Langmuir isotherm was developed by Irving Langmuir from 1916 to 1918 [7] to describe the dependence of the surface coverage on the pressure of a gas at a fixed temperature. There are many other types of isotherms (Temkin [9] p.250, Freundlich [9] p.247, ...) which differ in one or more of the assumptions made in deriving the expression for the surface coverage; in particular, on how they treat the surface coverage dependence of the enthalpy of adsorption. The first major assumption of Langmuir was that there are a fixed number of localized surface sites. The second was that adsorption takes place only at these specific sites and the saturation coverage corresponds to complete occupancy of these sites. Whilst the Langmuir isotherm is one of

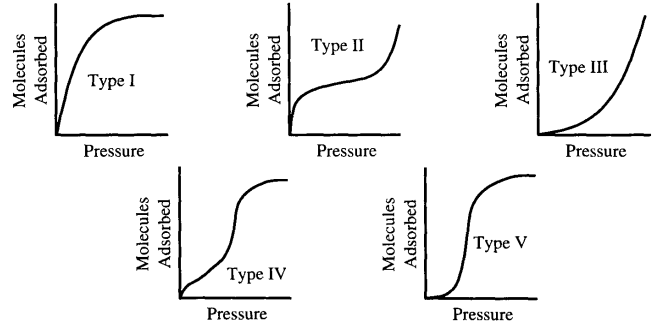


Figure 6: The five types of adsorption isotherms described by Brunauer

the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption.

In 1945, Brunauer proposed that one can classify the different kinds of behavior seen during the adsorption process into one of five general forms shown in figure 6.

- type I: The amount of gas increases with increasing pressure and then saturates at about a monolayer coverage
- type II: The amount of adsorbed gas increases with increasing pressure, starts to level off, and then starts to grow again at higher pressures to multi-layer coverage.
- type III: Initially there is very little adsorption, but once a small droplet or island of adsorbate nucleates on the surface, additional adsorption occurs more easily because of strong adsorbate-adsorbate interactions.
- type IV: Multilayers of gas adsorb onto the surface of the pores in a porous solid. Initially, the adsorption looks like a type II or a type III adsorption, but eventually the adsorbed layer gets so thick that it fills up the pores. No more gas can adsorb and the isotherm saturates.
- type V: Similar to type IV

We previously derived Langmuir's main result which was equation (13)

$$\theta = \frac{p}{p + p_0(T)} \quad . \quad (34)$$

where p_0 is a constant with respect to pressure, but depends on the temperature. It predicts that adsorption of a gas on a surface follows a type I adsorption isotherm. At low pressures the coverage varies linearly with pressure

$$\theta \simeq \frac{p}{p_0(T)} \quad \text{for } p \ll p_0(T) \quad . \quad (35)$$

However, the coverage saturates with increasing pressure and every site will almost be occupied.

$$\theta \simeq 1 \text{ for } p \gg p_0(T) . \quad (36)$$

Therefore if one wants to remove all adsorbed atoms from a surface, the solid has to be heated under low pressure.

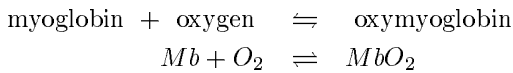
We also calculated the dissociative adsorption isotherm which was

$$\theta = \frac{\sqrt{p}}{\sqrt{p} + \sqrt{\tilde{p}_0(T)}} \quad (37)$$

The main difference to equation (34) is that at low pressure ($p \ll \tilde{p}_0(T)$) the coverage varies with \sqrt{p} .

7 Example: Adsorption of Oxygen

The result (34) describes important chemical and biological processes [5] p. 344. A good biochemical example is the reaction:



Myoglobin is an important protein which is found in muscles. For our purposes all we need to know is that each molecule of Mb can bind one molecule of oxygen. The reaction is studied in water solution.

We are interested in the fraction of myoglobin molecules that have bound an oxygen molecule. Let

- $[Mb]$ = concentration of myoglobin
- $[O_2]$ = concentration of oxygen
- $[MbO_2]$ = concentration of oxy-myoglobin

Then the desired fraction is

$$\theta = \frac{[MbO_2]}{[MbO_2] + [Mb]} = \frac{1}{\frac{[Mb]}{[MbO_2]} + 1} = \frac{[O_2]}{\frac{[Mb][O_2]}{[MbO_2]} + [O_2]} \quad (38)$$

which is of the form $\theta = c/(c_0 + c)$ as in equation (34), where now c is the concentration of oxygen molecules in solution water. Notice that the term $\frac{[Mb][O_2]}{[MbO_2]}$ that appears in the role of c_0 is made up of factors that are variable themselves. It must, therefore, be that this particular combination is in fact independent of the pressure and is a function only of the temperature. In figure 7 experimental results are compared to Langmuir's isotherm.

Historically, the classic work on the adsorption of oxygen by hemoglobin was done by Christian Bohr, the father of Niels Bohr.

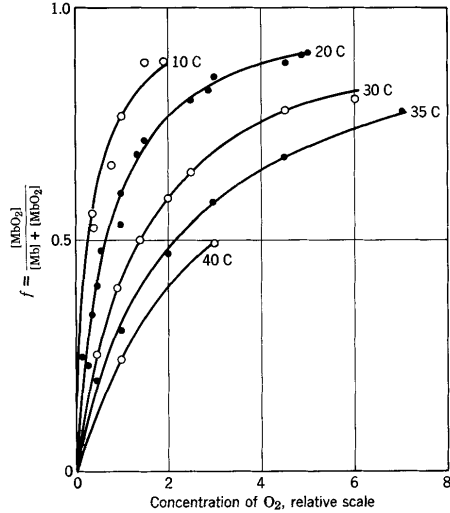


Figure 7: The reaction of a myoglobin molecule with oxygen may be viewed as an example of the adsorption of a molecule of O_2 at a site on the large myoglobin molecule. The results follow a Langmuir isotherm quite accurately. These curves show the fraction of myoglobin with adsorbed O_2 as a function of the partial pressure of O_2 at different temperatures.

8 Lattice gas models

The quantum mechanics of chemisorption relies fairly heavily on the concept of a lattice gas. The starting point for a lattice gas is a Hamiltonian which is isomorphic with magnetic Hamiltonians, such as the Ising model [11], which was solved exactly in two dimensions by Onsager in 1944. As with all these models, they provide an explicit solution to a well-posed question. The simplest spin-1/2 Hamiltonian is

$$\mathcal{H} = -H \sum S_i - J_{ij} \sum S_i S_j + \dots \quad (39)$$

where the magnetic field H biases the occupation of a particular site, equivalent to $-(E_a + \mu)$. The exchange interaction J_{ij} is the interaction between neighbors i and j and is equivalent to the lateral interaction in a nearest neighbor model. The spin S_i corresponds to the occupation of a site if $S_i = +1/2$, or an empty site if $S_i = -1/2$; these correspondences are clearly conventions since the model is symmetric in the spin variables. Connection with thermodynamics is made via the general relation

$$F = -kT \ln(\text{Tr} \exp(-\mathcal{H}/kT)) \quad (40)$$

where the trace is the sum of the diagonal elements of the Hamiltonian matrix \mathcal{H} . There is thus a major theory industry in constructing and solving such models, both with analytic solutions and with Monte Carlo simulations. These models are most reasonable for strong

chemisorption, where we have a very site-specific bond, and where lateral interactions are considerably smaller. The phase diagrams constructed via this simplest equation exhibit particle-hole symmetry; assuming the saturation coverage in the Langmuir isotherm is defined as $\theta = 1$, then coverages of θ and $1 - \theta$ are equivalent and the (T, θ) phase diagram is symmetric about $\theta = 1/2$. Extra terms can be added via two, or three body interactions of the form

$$\mathcal{H}_1 = \sum J_{ijk} S_i S_j S_k \quad (41)$$

Such higher order interactions allow lower symmetry phase diagrams to emerge.

A detailed account of higher order interactions in the context of lattice gas models is given by Ted Einstein (1996) [4]. This Einstein is alive and well and working at the University of Maryland.

9 Discussion

In the previous section we examined some simple models for adsorption. Following the way of Langmuir even such simple models can describe results of complex experiments: Langmuir's main result was equation (34) which fits even adsorption of molecular oxygen to myoglobin, which is similar to haemoglobin and also important for the transport of oxygen in blood circulation. Nowadays much research is done with Monte Carlo simulation because of much less needed calculation time with modern computers.

We obtained a little different result for the model of adsorption with dissociation. But it was of type I, too. This process is very important for catalyst effects. A statistical thermodynamic model of the adsorption of a metal surface was given by Bernard and Lupis in 1974 [8].

The adsorption and recombination of hydrogen on a model graphite surface [1] has also recently been calculated with an iterative program. The main result was that hydrogen atoms are found to be chemisorbed at a site with a zero-point binding energy of $0.7eV$ and at an equilibrium distance of 2.25 \AA above the site. Despite a barrier of about $0.4eV$ between adjacent sites, calculations suggest that at temperatures as low as $10 K$, an atom will tunnel through to adjacent sites. Experimental results show that the region in which H_2 begins to form exhibits a repulsive potential. Energy released during incipient bonding must be quickly transferred to the surface otherwise the newly formed H_2 will dissociate.

Other research has been done in the theory of sticking [6]. A generalization of a lattice gas model is used to study the coverage and temperature dependence of the sticking coefficient. **Sticking** is a process where an incident molecule collides with a surface and then bounces around until it finds a site where it can adsorb.

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