31.6: Atoms and Molecules can Physisorb or Chemisorb to a Surface

In this section, we will consider both the energetics of adsorption and factors which influence the kinetics of adsorption by looking at the "potential energy diagram/curve" for the adsorption process. The potential energy curve for the adsorption process is a representation of the variation of the energy (PE or E) of the system as a function of the distance (d) of an adsorbate from a surface.

Within this simple one-dimensional (1D) model, the only variable is the distance (d) of the adsorbing molecule from the substrate surface (Figure 31.6.1).
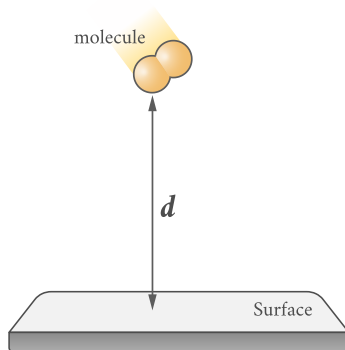

Figure 31.6.1: A particle approaching a solid surface. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy of the system is a function only of this variable i.e.

$$E = E(d)$$

It should be remembered that this is a very simplistic model which neglects many other parameters which influence the energy of the system (a single molecule approaching a clean surface), including for example

- *the angular orientation of the molecule*
- *changes in the internal bond angles and bond lengths of the molecule*
- *the position of the molecule parallel to the surface plane*

The interaction of a molecule with a given surface will also clearly be dependent upon the presence of any existing adsorbed species, whether these be surface impurities or simply pre-adsorbed molecules of the same type (in the latter case we are starting to consider the effect of surface coverage on the adsorption characteristics). Nevertheless, it is useful to first consider the interaction of an isolated molecule with a clean surface using the simple 1D model. For the purposes of this section, we will also not be overly concerned whether the "energy" being referred to should strictly be the internal energy, the enthalpy or free energy of the system. We will also make a distinction between physisorption and chemisorption. These two types of interaction with a surface are differentiated by the strength of interaction bewteen the adsorbed particle and the surface. A physisorbed particle will always be farther away from the surface than an identical particle that is chemisorbed (Figures 31.6.2 and 31.6.3).
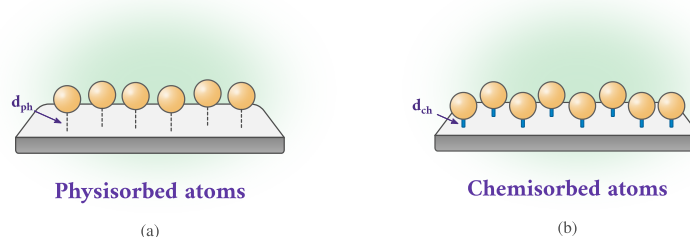

Figure 31.6.2: a) A picture of physisorbed atoms. The atoms are, on average, a distance of d_{ph} from the surface. b) A picture of chemisorbed atoms. The atoms are, on average, a distance of d_{ch} from the surface. Note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)
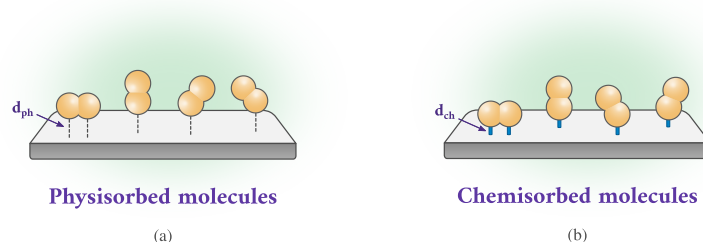
Figure 31.6.3: a) A picture of physisorbed molecules. The molecules are, on average, a distance of d_{ph} from the surface. Note that the molecules can adsorb to the surface at various orientations. b) A picture of chemisorbed molecules. The molecules are, on average, a distance of d_{ch} from the surface. Note that the molecules can adsorb to the surface at various orientations. Also note that d_{ph} is always greater than d_{ch}. (CC BY-NC; Ümit Kaya via LibreTexts)

CASE I - Physisorption

In the case of pure physisorption, e.g., Ar/metals, the only attraction between the adsorbing species and the surface arises from weak, van der Waals forces. As illustrated in Figure $31.6.4$ below, these forces give rise to a shallow minimum in the PE curve at a relatively large distance from the surface (typically $d > 0.3\,nm$) before the strong repulsive forces arising from electron density overlap cause a rapid increase in the total energy.
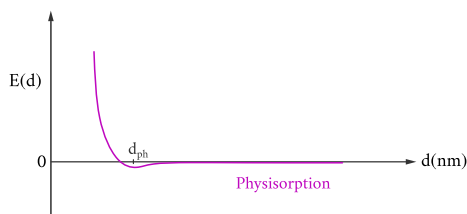

Figure 31.6.4: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

There is no barrier to prevent the atom or molecule which is approaching the surface from entering this physisorption well, i.e. the process is not activated and the kinetics of physisorption are invariably fast.

CASE II - Physisorption + Molecular Chemisorption

The weak physical adsorption forces and the associated long-range attraction will be present to varying degrees in all adsorbate/substrate systems. However, in cases where chemical bond formation between the adsorbate and substrate can also occur, the PE curve is dominated by a much deeper chemisorption minimum at shorter values of d, as shown in Figure $31.6.5$.
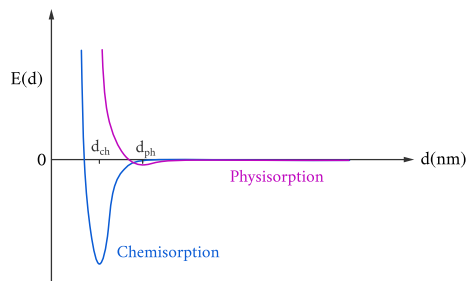

Figure 31.6.5: A graph showing the potential energy change as a particle moves closer and closer to a surface to eventually either physisorb or chemisorb onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

The graph above shows the PE curves due to physisorption and chemisorption separately. In practice, the PE curve for any real molecule capable of undergoing chemisorption is best described by a combination of the two curves, with a curve crossing at the point at which chemisorption forces begin to dominate over those arising from physisorption alone (Figure 31.6.6).
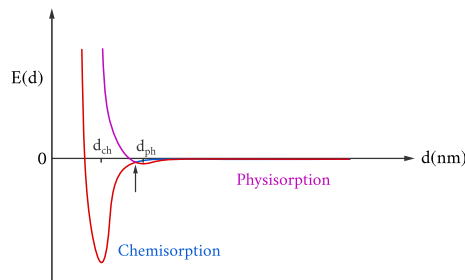
Figure 31.6.6: The red curve is a graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorbing onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The vertical arrow points to the crossover point at which the particle approaches close enough to the surface for the forces of chemisorption to dominate. (CC BY-NC; Ümit Kaya via LibreTexts)

The minimum energy pathway obtained by combining the two PE curves is now highlighted in red. Any perturbation of the combined PE curve from the original, separate curves is most likely to be evident close to the highlighted crossing point.

For clarity, we will now consider only the overall PE curve as shown in Figure 31.6.7:
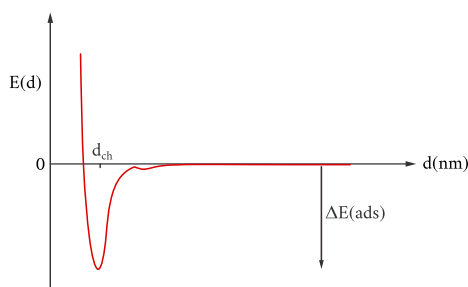
Figure 31.6.7: A graph showing the potential energy change as a particle moves closer and closer to a surface, eventually physisorbing onto the surface, and then undergoing chemisorption onto that same surface. The distance d_{ch} is the equilibrium bond distance of lowest potential energy for the chemisorbed particle. The energy of adsorption is represented by $\Delta E(ads)$. (CC BY-NC; Ümit Kaya via LibreTexts)

The depth of the chemisorption well is a measure of the strength of binding to the surface. In fact, it is a direct representation of the energy of adsorption, whilst the location of the global minimum on the horizontal axis corresponds to the equilibrium bond distance (d_{ch}) for the adsorbed molecule on this surface.

The energy of adsorption is *negative*, and because it corresponds to the energy *change* upon adsorption, it is better represented as ΔE (ads) or ΔE_{ads}. However, you will also often find the depth of this well associated with the enthalpy of adsorption, ΔH (ads).

> *The "heat of adsorption", Q, is taken to be a positive quantity equal in magnitude to the enthalpy of adsorption ; i.e. Q = -ΔH(ads))*

In this particular case, there is clearly no barrier to be overcome in the adsorption process and there is no activation energy of adsorption (i.e. $E_a^{ads} = 0$, but do remember the previously mentioned limitations of this simple 1D model). There is of course a significant barrier to the reverse, desorption process; the red arrow in Figure 31.6.8 below represents the activation energy for desorption.
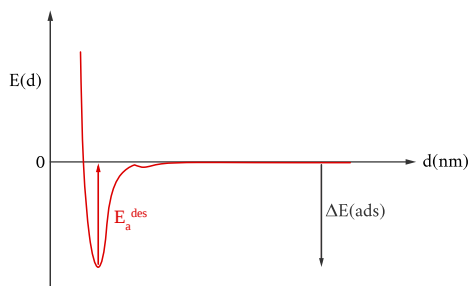
Figure 31.6.8: A graph showing both the energy of adsorption, $\Delta E(ads)$, and the activation energy of desorption, E_a^{des}. (CC BY-NC; Ümit Kaya via LibreTexts)

Clearly, in this particular case, the magnitudes of the energy of adsorption and the activation energy for desorption can also be equated i.e.

$$E_a^{des} = \Delta E(ads)$$

or

$$E_a^{des} \approx -\Delta H(ads)$$

CASE III - Physisorption + Dissociative Chemisorption

In this case, the main differences arise from the substantial changes in the PE curve for the chemisorption process. Again, we start off with the basic PE curve (Figure $31.6.9$) for the physisorption process which represents how the molecule can weakly interact with the surface :
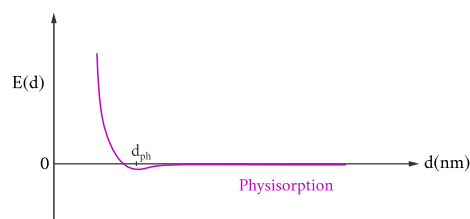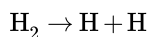

Figure 31.6.9: A graph showing the potential energy change as a particle moves closer and closer to a surface and eventually physisorbs onto that surface. The distance d_{ph} is the equilibrium interaction distance of lowest potential energy for the physisorbed particle. (CC BY-NC; Ümit Kaya via LibreTexts)

If we now consider a specific molecule such as H_2 and initially treat it as being completely **isolated** from the surface (i.e. when the distance, d, is very large), then a substantial amount of energy would need to be put into the system in order to cause dissociation of the molecule.

$$H_2 \rightarrow H + H$$

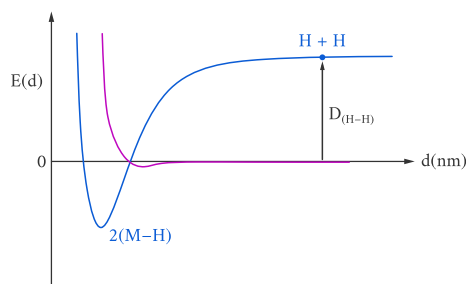This amount of required energy is the bond dissociation energy $D_{(H-H)}$, which is some 435 kJ mol^{-1} or 4.5 eV.

Figure 31.6.10: A graph showing the potential energy changes involved in the dissociation of an H2 molecule. An H2 molecule very far away from the surface has two paths by which it can end up as two separate H atoms chemisorbed onto the surface. (a) An input of 435 kJ per mole will break of the H-H bond. The separate H atoms can then eventually approach the surface and bond to it. (The red pathway) (b) The H2 molecule can approach the surface, physisorb onto the surface, and then undergo dissociative chemisorption. (Starting on the right on the purple pathway, then switching to the red pathway at the crossover point.) (CC BY-NC; Ümit Kaya via LibreTexts)

The red dot in Figure 31.6.10 above thus represents two hydrogen atoms, equidistant (and a long distance) from the surface, and also now well separated from each other. If these atoms are then allowed to approach the surface they may ultimately both form strong chemical bonds to the substrate. This possible bonding of two H atoms to the surface (shown as 2(M-H) in the Figure) corresponds to the minimum in the red curve which represents the chemisorption PE curve for the two H atoms.

In reality, of course, such a mechanism for dissociative hydrogen chemisorption is not practical; the energy down payment associated with breaking the H-H bond is far too severe. Instead, a hydrogen molecule will initially approach the surface along the physisorption curve. If it has sufficient energy it may pass straight into the chemisorption well ("direct chemisorption") as shown below in Figure 31.6.11
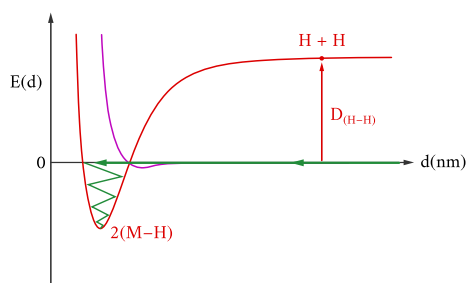

Figure 31.6.11: A graph showing the potential energy changes involved in the direct chemisorption of an H2 molecule. The H2 molecule approaches the surface following the green pathway, bypasses physisorption, and instead undergoes direct dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

Alternatively, the hydrogen molecule may first undergo transient physisorption, a state from which it can then either desorb back as a molecule into the gas phase or cross over the barrier into the dissociated, chemisorptive state (as illustrated *schematically* in Figure 31.6.12).
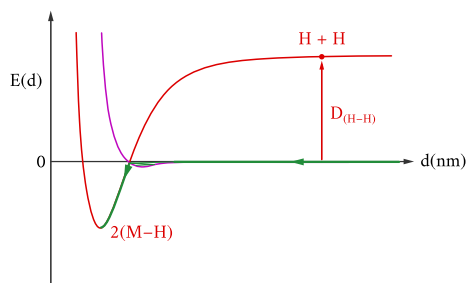

Figure 31.6.12: A graph showing the potential energy changes involved in the precursor-mediated chemisorption of an H_2 molecule. The H_2 molecule approaches the surface following the green pathway, first undergoes physisorption, and then undergoes dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

In this latter case, the molecule can be said to have undergone "precursor-mediated" chemisorption. A picture of the process of the approach, physisorption, and dissociative chemisorption of a molecule is shown in Figure 31.6.13 The molecule in this picture is

following the general potential energy pathway described in either Figure $31.6.11$or Figure $31.6.12$
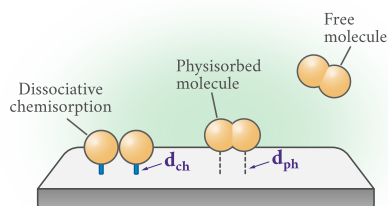

Figure 31.6.13: The sequential process of a free molecule approaching a surface, becoming physisrobed onto the surface, and eventually undergoing dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

The characteristics of this type of dissociative adsorption process are clearly going to be strongly influenced by the position of the crossing point of the two curves (molecular physisorption versus dissociative chemisorption) - relatively small shifts in the position of either of the two curves can significantly alter the size of any barrier to chemisorption.

In the example shown in Figure $31.6.14$below there is no direct activation barrier to dissociative adsorption - the curve crossing is below the initial "zero energy" of the system.
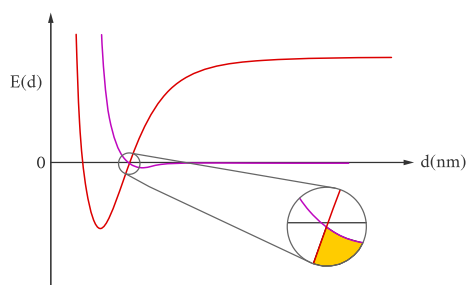

Figure 31.6.14: The potential energy pathway for physisorption followed by dissociative adsorption in which there is no direct activation barrier. (CC BY-NC; Ümit Kaya via LibreTexts)

In the case shown in Figure $31.6.15$, there is a substantial barrier to chemisorption. Such a barrier has a major influence on the **kinetics** of adsorption.
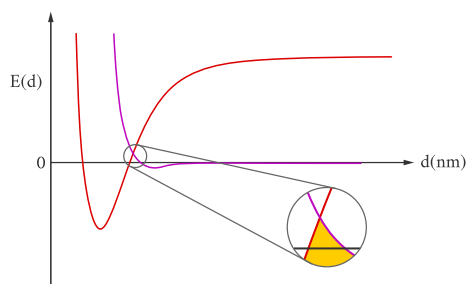

Figure 31.6.15: The potential energy pathway for physisorption followed by dissociative adsorption in which there is an activation barrier. ((CC BY-NC; Ümit Kaya via LibreTexts)

The depth of the physisorption well for the hydrogen molecule is actually very small (in some cases negligible), but this is not the case for other molecules and does not alter the basic conclusions regarding dissociative adsorption that result from this model; namely that the process may be either activated or non-activated depending on the exact location of the curve crossing.

At this point, it is useful to return to consider the effect of such a barrier on the relationship between the activation energies for adsorption and desorption, and the energy (or enthalpy) of adsorption.
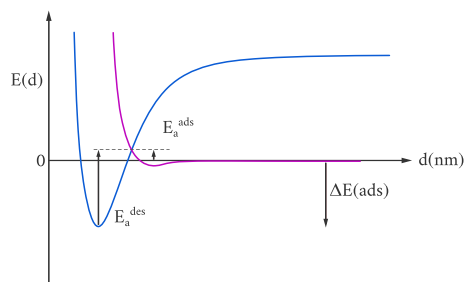
https://chem.libretexts.org/@go/page/14578

Figure 31.6.16: A comparison of the activation energy of adsorption E_a^{ads}, the activation energy of desorption E_a^{des}, and the energy of adsorption for a molecule that undergoes physisorption, directly followed by dissociative chemisorption. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 31.6.16,

$$E_a^{des} - E_a^{ads} = -\Delta E_{ads}$$

but, because the activation energy for adsorption is nearly always very much smaller than that for desorption, and the difference between the energy and the enthalpy of adsorption is also very small, it is still quite common to see the relationship

$$E_a^{des} \approx -\Delta H_{ads}$$

For a slightly more detailed treatment of the adsorption process, you are referred to the following examples of More Complex PE Curves & Multi-Dimensional PE Surfaces.

Contributors and Attributions

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