way as they are produced for LEED. Unfortunately, HAS is far more difficult to perform technically and is very expensive (the apparatus required for HAS is described in Chapter 4, Section 4.6.2). It is also necessary to have surfaces which are highly ordered; usually, surfaces must be ordered to a far greater degree than those from which LEED patterns can be obtained. This is a result of the 'coherence' properties of the incident beams of He atoms and electrons. A helium beam is coherent (i.e. has the same phase) over a wider area than a typical electron beam, which means that the diffraction features observed for HAS arise from a larger area of surface than those obtained in LEED. Any disorder in this area of surface causes destructive interference. The effect is greater on HAS compared to LEED simply because of the larger total amount of disorder within the area being sampled.

However, despite these problems this technique has proved very informative for elucidating several important problems in surface science.

(iii) ‘Fitting’ data to obtain surface structures

The usual way in which the deduction of a structure is carried out is by an iterative fitting process. Typically, an educated guess at the real space structure is made and this is fed into a computer package that is designed for the task. The program then calculates the reciprocal mesh and the intensity pattern that would result from the proposed structure. The generated reciprocal pattern is compared with the observed pattern, usually using some kind of ‘least-mean-squares’ fitting procedure. If the data are statistically ‘close’ to the suggested structure, it is assumed to be the correct one. If the data are not ‘close’ enough, a new ‘refined’ structure is suggested. The reciprocal mesh and its intensity are then generated for the new structure and this is compared again to the observed structure. The whole process continues until the ‘fit’ is judged to be statistically close enough to describe the structure.

The computer packages used encompass the ‘best’ type of scattering theory for the technique used. In the case of HAS, a kinematic package is used, while for LEED, packages with time-consuming and complex dynamic theory are used.

3 Adsorption and desorption

3.1 Adsorption processes

3.1.1 Atomic/molecular collisions with surfaces

There are several possible outcomes when an atom or a molecule hits a surface. The first is that the atom or molecule merely bounces back off the surface. This is called 'elastice scattering', as in this mechanism there is no energy exchange between the surface and the incident atom or molecule. This is essentially the process that occurs when helium atoms are scattered from surfaces in HAS experiments, as described in Chapter 2.

A second possibility is that as an atom or a molecule rebounds from the surface, it loses or gains energy in an 'inelastic scattering' process. This can be likened to the Raman scattering process where the incident photons lose or gain quanta of vibrational and/or rotational energy.

Both of these outcomes can be used to our advantage in the development of techniques for studying surface phenomena (such as HAS), but the outcome of an atomic or a molecular collision that results in the retention of the molecule on the surface is of far greater importance to our study of surface chemistry. There are two types of interactions that can occur. In broad terms these are physical adsorption (or physisorption) and a much stronger interaction, which results in the formation of one or more chemical bonds between the adsorbed molecule and the surface (chemisorption). In each case the atom or molecule being adsorbed on the surface is usually described as the adsorbate; the adsorbing surface is usually termed the adsorbent or substrate.

3.1.2 Coverage

The coverage, $\theta'$, of adsorbate on the surface is defined as

$$\theta' = \frac{N_{\text{ads}}}{N_s}$$

(3.1)

where $N_{\text{ads}}$ is the number of adsorbate atoms per unit area and $N_s$ is the number of surface atoms per unit area. This expression can be used to compare the number of atoms or molecules directly adsorbed on the surface in the first layer with the number
of atoms in the surface. Another way of describing the amount of adsorbate on the surface is by using the fractional coverage, \( \theta \), which is given

\[
\theta = \frac{N_{\text{ads}}}{N_{\text{m}}}
\]

(3.2)

where \( N_{\text{m}} \) is the number of atoms/molecules adsorbed per unit area to produce one complete layer on the surface. The maximum amount of adsorbate which is adsorbed in the first layer is usually called a monolayer, so \( \theta = 1 \), on the other hand, is commonly less than 1, as for example, when the adsorbed molecule is larger than the substrate atoms. (On some occasions the coverage \( \theta \) can be found to be greater than 1: for adsorption of HI on W, for example, it is 2, because two H atoms can be adsorbed on each W atom.)

3.1.3 Physisorption

Physisorption involves the balancing of a weak attractive force, for example, of a Van der Waals nature, between the surface and the adsorbate, with the repulsive force associated with close contact. The process is always exothermic and the energy given out on adsorption, the heat of adsorption, \( \Delta H_{\text{ads}} \), is low, typically in the region –10 to –40 kJ mol\(^{-1}\). In these systems the adsorbate–adsorbate interactions are often comparable with and can be considerably greater than, the adsorbate–surface interactions. (This will be dealt with in greater detail in Chapter 5).

A Van der Waals interaction can be described approximately by the Lennard-Jones (12-6) potential as for molecule–molecule interactions, for which the potential energy \( V(r) \), is given by

\[
V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(3.3)

where \( r \) is the interatomic distance, \( \varepsilon \) is the well-depth of the potential energy curve and \( \sigma \) is the interatomic distance at which the potential energy curve crosses zero. The origin of the parameters in eqn (3.3) comes from the attractive interaction between atoms/molecules which has the \( 1/r^6 \) dependence and the repulsive interaction which has a \( 1/r^{12} \) dependence.

The repulsive forces become significant as the atoms/molecules approach each other closely. At the equilibrium bond distance the repulsion between electron clouds just balances the attractive forces and at this point the curve crosses the zero in energy \( V(r) \).

The attractive forces are due to a combination of dispersion and dipolar forces. For a molecule approaching a surface, dispersion forces arise from instantaneous fluctuations in electron density which cause transient dipoles in the molecule; these interact with their opposite numbers in the surface atoms. Forces due to molecules that have permanent dipole moments are usually stronger. These permanent dipoles interact with electrical asymmetries in the surface. The presence of permanent dipoles can also induce dipoles in polarizable non-polar molecules and in polarizable surfaces.

The situation when a molecule approaches a surface is more complex than that which occurs when two atoms/molecules approach each other. The potential energy can be calculated as a function of distance between surface and adsorbing molecule by a pairwise summation of all interactions between the incoming molecule and the nearest solid atoms. The incoming molecule interacts with each of the atoms in the solid and each of these interactions can be described by a Lennard-Jones (12-6) pair potential. Summing the pair potentials of the adsorbing molecule with each atom in the solid leads to an expression of the form given in eqn (3.4), where the potential energy is given as a function of the height of the molecule above the surface, \( z \).

\[
V(z) = 4\pi \varepsilon N_{\text{m}} \sigma^2 \left[ \frac{1}{45} \left( \frac{\sigma}{r} \right)^{12} - \frac{1}{6} \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(3.4)

For physisorption, the strength of interaction is greater than that which is found in other weakly interacting systems because the interaction with each volume element in the solid is taken into account. This means that a 9–3 potential applies rather than a 12–6 potential. The 9–3 potential is plotted in Fig. 3.1, with the parameters used indicated on the figure. The molecule adopts an equilibrium height above the surface which corresponds to the minimum of the potential well, \( z \), and this well depth is the heat of adsorption, \( \Delta H_{\text{ads}} \). \( \Delta H_{\text{ads}} \) is sometimes called \( q \), where \( q = -\Delta H_{\text{ads}} \). This nomenclature was adopted for convenience because \( q \) is always positive but it is slowly falling into disuse.

Generally speaking, physisorption is non-specific and any atom or molecule can adsorb on any surface under appropriate experimental conditions (i.e. temperature and pressure); large amounts of physisorption are favoured when the surface is at low temperature. The heat of adsorption is usually of the same order of magnitude but slightly larger than the latent heat of condensation of the adsorbate molecules.

3.1.4 Chemisorption

Chemisorption describes the process by which a strong chemical bond is formed between the surface and the adsorbate. It involves the exchange of electrons between the adsorbing molecule and the surface. The heats of adsorption for chemisorption are generally larger than for physisorption; some are very large. \( \Delta H_{\text{ads}} \) tends to be in the range –40 to –1000 kJ mol\(^{-1}\) and it is found that chemisorbed layers with large heats of adsorption tend to be very stable to high temperatures. The bonds formed may be ionic or covalent, or a mixture of the two. Chemisorption differs markedly from
physisorption in that there is usually a high degree of specificity in the interaction of different adsorbates with different substrate surfaces. With a crystalline adsorbent, the strength of adsorption is usually dependent on which face is exposed.

From simple thermodynamic considerations,

\[ \Delta G = \Delta H - T \Delta S \]  

so that the free energy change \( \Delta G \) must be negative. Upon adsorption onto a surface, most of the translational, and often the rotational, degrees of freedom are lost, and so the order of the system is increased. This means that the entropy change, \( \Delta S \), is always negative. As the absolute temperature \( T \) is positive, it follows that \( \Delta H_{\text{ads}} \) has to be negative; thus, in order to proceed, the chemisorption process must be exothermic.

Several factors might cause a strong coverage dependence for \( \Delta H_{\text{ads}} \). For physisorbed species it can vary because of the effect of electrical polarization which changes as the adsorbates become more closely packed on the surface. In the case of chemisorbed species, the charge transfer between surface and adsorbate can cause later adsorption to be less energetically favourable. Additional effects can be due to electrostatic coupling between adsorbates or repulsive forces which occur when the chemisorbed species are packed closely on the surface. For this reason \( \Delta H_{\text{ads}} \) is always quoted for a given coverage of adsorbate on the surface.

Chemisorption resulting in the formation of a chemical bond between the adsorbing molecule and the surface is termed non-dissociative chemisorption; this applies when all the original interatomic bonds of the adsorbed molecule are retained in some form. Adsorption can, alternatively, result in the dissociation of the molecule on binding to the surface. Chemisorption in this manner frequently requires activation. Chemisorption processes can be described by potential energy curves for non-dissociative and dissociative processes as detailed below.

It should be noted here that for chemisorption, while the bonding between adsorbate and substrate can be represented by the Lennard-Jones (12-6) potential, it can alternatively be represented by a Morse curve (as used in diatomic molecular spectroscopy).

3.1.4.1 Non-dissociative chemisorption

The non-dissociative chemisorption process for molecule \( AB \) can be written

\[ AB \rightarrow AB_{\text{ads}} \]  

The potential energy curve, which is based on a Lennard-Jones (12-6) potential, \( V(z) \), is shown in Fig. 3.2. The distance between the adsorbing molecule and the surface, \( z \), is presented on the \( z \)-axis. The potential for the weakly bound physisorption state is shown as a dashed line and that for the chemisorption well as a solid line. As the molecule approaches the surface it drops into the weakly bound (often short-lived) physisorbed precursor state, then passes over a small energy barrier and into the chemisorption well as shown by the solid curve in the figure.

An example of this sort of chemisorption is of CO adsorption on low indexed copper surfaces.

![Fig. 3.2 The non-dissociative chemisorption potential energy curve. The physisorption state is shown by a dashed curve and the lowest energy pathway is shown as a solid line.](image_url)

3.1.4.2 Dissociative chemisorption

As indicated above, there are two forms of dissociative chemisorption: activated processes requiring additional energy and non-activated which proceed because they are energetically favourable. In this case we will consider the simple dissociation

\[ AB \rightarrow A_{\text{ads}} + B_{\text{ads}} \]  

(i) Activated dissociative chemisorption

The potential energy curve for activated dissociative chemisorption is shown in Fig. 3.3. Here the curve with a dashed section shows the physisorption of \( AB \) on the surface. It crosses the dashed-dotted curve, which shows the interaction of the \( A + B \) fragments with the surface. The important point to note here is that the two curves cross above the zero of potential energy. The minimum energy pathway is shown as a solid curve. In the absence of additional energy the molecule is adsorbed in the physisorption well. The molecule can only cross over into the dissociated chemisorption state if additional energy is supplied to overcome the activation barrier, which is above the zero in potential energy.

(ii) Non-activated dissociative chemisorption

The potential energy curves for non-activated dissociative chemisorption are shown in Fig. 3.4. The curves representing physisorbed \( AB \) and chemisorbed \( A + B \) fragments are essentially the same as those for the activated process in Fig. 3.3, but in this case the
two curves cross just below the zero of potential energy. Thus, no additional energy is needed to pass the system into the dissociated chemisorbed state. In order to gain a mental picture of the adsorption states, idealized representations of the adsorption states for hydrogen adsorbing on nickel are also shown in the figure, associated with $z$. Initially a physisorbed precursor state is formed and the molecule then forms a higher energy transition state, at the top of the activation energy barrier $E_a$, before finally passing into the chemisorption potential well.

A good example of dissociative chemisorption is that of $H_2$ adsorption on a metal surface. When a diatomic molecule nears a surface, an equilibrium as given in eqn (3.8) is set up:

$$M + H_{2g} \leftrightarrow 2M + H_{2h}$$  \hspace{2cm} (3.8)

The position of the equilibrium depends on the reaction conditions, particularly in terms of pressure and temperature. As we have seen earlier, $\Delta H_{ads}$ must be negative for the dissociation to proceed and this condition is met when $2 \times D_{H-H} > D_{M-H}$, where $D$ denotes the dissociation energies of the $M-H$ and $H-H$ species, respectively. From eqn (3.5) it can be seen that when $\Delta H_{ads}$ is small, the position of the equilibrium is strongly dependent on $T$.$\Delta S$. Whether or not the process is activated is governed by the precise energetics involved as the molecule approaches the surface.

A striking example of this is the dissociative adsorption of molecular hydrogen on copper. At a pressure of $10^{-6}$ mbar and at room temperature, negligible quantities of atomic hydrogen are adsorbed. However, at the same temperature, a pressure of 100 mbar produces a monolayer of $\text{Cu-H}$ species on the surface.

Dissociated species appear generally at higher temperatures than non-dissociated species because the system has to be carried over the activation energy barrier to dissociation for both activated and non-activated dissociative chemisorption.

The three situations are described here in only schematic, one-dimensional representations and are, in any case, very simple systems. In more complex systems there are often several possible precursor states to chemisorption, and much closer similarity between energies of the non-dissociated and dissociated states which are in competition. This often makes the possibilities within the adsorption process more complicated.

3.1.5 Adsorption dynamics and the potential energy hypersurface

Figure 3.5(a) shows the conventional schematic diagram for the potential energy curves for the dissociative adsorption of molecule $AB$ on a surface (from Fig. 3.3). The energy is drawn as a function of a one-dimensional pathway. As we noted in the
Fig. 3.5 The dynamics of surface processes. (a) the 1-d potential energy curve for activated dissociative adsorption (from Fig. 3.3) and (b) a 2-d representation of the same process, the potential energy hypersurface.

previous section, although the curve gives a simple picture of the energetics involved in adsorption, it is not particularly useful for obtaining anything more than a very qualitative understanding of the adsorption/desorption process, or for making overall predictions about the adsorption process. Such phenomena require more complex consideration.

Figure 3.5(b) shows a view of the same process, plotted as a function of two reaction parameters, which gives far better insights into the details of the atomic motions of the surface and adsorbates, the so-called dynamics of the adsorption process. This form of plot is called a potential energy hypersurface and such plots are commonly produced to describe gas-phase chemical adsorption dynamics. The contours show lines of equal energy and the two dashed lines show the cuts across the potential energy hypersurface which correspond to the 1-d curves in Fig. 3.5(a). The arrows indicate the pathway of minimum energy between the two states. From the 2-d plot we can begin to understand how a concerted mechanism for dissociation is required; in other words how, as the AB bond weakens, the surface bond strengthens.

The translational and vibrational energies involved are very important and their effects are illustrated in Fig. 3.6 which shows the energies related to the molecular interatomic distance, \( a \), and molecular height, \( z \), from the surface. There are two characteristic reaction scenarios which are commonly found, shown in Fig. 3.6(a) and (b). The transition state is indicated by the 'seam' at the point at which it crosses the minimum energy pathway. In the first example, Fig. 3.6(a), this seam sits in the 'entrance channel' which describes the situation when the molecule is not stretched as it leaves the physisorption well and moves in towards the surface. Thus the bond length of the transition state species is not significantly different to that of the precursor. If the translational kinetic energy is increased at this stage, the rate of dissociation is increased.

The other scenario is shown in Fig. 3.6(b). In this case, the adsorbate is closer to the surface as it sits in a physisorption well for which the adsorbate-substrate distance is close to that adopted by the molecular fragments once they have dissociated. Vibration of the physisorbed molecule (which causes an increase in the interatomic distance) then leads to dissociation and provides the rate-limiting barrier. The transition state is said to lie in the 'exit channel', and any increase in translational energy has little effect on the dissociation process. An increase in vibrational energy, on the other hand, promotes the dissociation (called 'vibrationally assisted sticking').
This 2-d picture, while being of far greater value than the 1-d picture, is also oversimplified, because it does not depict enough degrees of freedom. Even in the case of dissociation of a diatomic molecule there are six degrees of freedom for the molecule as it interacts with a static substrate. Effectively, what we see with the 2-d plot is the chosen freezing out of most of the possible coordinates, as we look at slices through this complex multidimensional space.

### 3.1.6 Comparison of chemisorption and physisorption

It is useful to have a summary to compare the chemisorption and physisorption processes in order to help to distinguish between them.

<table>
<thead>
<tr>
<th>Chemisorption</th>
<th>Physisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\Delta H_{0a} )</td>
<td>( -10-40 \text{ kJ mol}^{-1} )</td>
</tr>
<tr>
<td>Kinetics of activation</td>
<td>Non-activated</td>
</tr>
<tr>
<td>Number of layers</td>
<td>One monolayer (assuming no reconstruction or incorporation of adsorbate into the subsurface region)</td>
</tr>
<tr>
<td>Chemical reactivity</td>
<td>Can cause reactivity changes in the adsorbate</td>
</tr>
<tr>
<td>Specificity</td>
<td>Normally dependent on specific adsorbate-surface interactions</td>
</tr>
</tbody>
</table>

### 3.1.7 Work function change associated with adsorption

The work function of a clean surface was discussed in Chapter 2, Section 2.2.2. Adsorption on the surface causes a change in the observed work function, even if the interaction is that of weak physisorption. The change in work function, \( \Delta \phi \), is given by

\[
\Delta \phi = \phi_{\text{ads}} - \phi_{\text{clean}} \quad (3.9)
\]

where \( \phi_{\text{ads}} \) is the work function of the adsorbate-covered surface at a given coverage \( \theta \) or \( \theta' \), and \( \phi_{\text{clean}} \) is the work function of the clean surface. The change in the work function is a valuable parameter for assessing the degree of charge redistribution following adsorption.

The distribution of the charge on the surface or surface dipole has considerable influence on the atoms or molecules that adsorb. It can affect the molecular shape and orientation adopted on the surface and can lead to fragmentation of the adsorbate. The field at the surface even affects inert gas atoms such as Ar and Xe as they are polarizable, and so dipoles are produced within the atoms themselves during adsorption.

The effect of inert gas adsorption on the work function is not what might be expected from a naive, classical prediction. In Section 2.2.1 it was seen that the electron density of the clean surface spills out towards the vacuum. In the classical picture, the electrons of the incoming atoms would be repelled by the surface such that a dipole would be set up within them, with the positive end closest to the surface. This would cause an increase in the work function because the dipoles set up in the atoms would add to the charge at the surface.

However, the observed effect is that a decrease in work function occurs, which shows that the inert gas atoms are polarized in the opposite direction, where a negative charge builds up between the atoms and the surface. The reason is concerned with a subtle effect due to a quantum mechanical electron correlation effect. This arises because the electrons can attain lower energies by behaving cooperatively with the free electrons in the metal; they therefore have a preference to move to a region of higher electron density. This phenomenon cannot be understood classically.

The resulting arrangement of adsorbed atoms and their dipoles is shown schematically in Fig. 3.7 for physisorbed Ar on a metal surface.

The situation can be modelled as a parallel plate condenser and so the Helmholtz equation can be applied. This is given in eqn (3.30) where \( \Delta V \) is the change in surface potential, \( \mu \) is the induced dipole moment, which is taken by convention to be positive in the \( + \rightarrow - \) direction, and \( \varepsilon_0 \) is the permittivity of free space (about \( 8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1} \)):

\[
\Delta V = \frac{N_{\text{ads}} \mu}{\varepsilon_0} \quad (3.10)
\]

The change in surface potential is related to the work function change by

\[
\Delta \phi = \Delta V e \quad (3.11)
\]

where \( e \) is the charge on the electron. A measurement of \( \Delta V \) or \( \Delta \phi \) can therefore be used to give an estimate of the partial charge on the adsorbate, \( Q \), because

\[
\mu = Q e \quad (3.12)
\]

where \( \alpha \) is the separation of the adsorbate and the screening charge.

Chemisorption often causes large changes in the observed work function. This is because there is usually a high degree of charge transfer between the adsorbate and the surface when strong chemical bonds are formed. Intuitively, one can predict that adsorbates which are electropositive with respect to the surface will have the opposite effect on \( \phi \) compared to the electronegative ones. The way in which they affect \( \phi \) depends also on the 'double charge layer' which is induced by the surface itself (as discussed in Section 2.2.2). Figure 3.8 shows a schematic energy level diagram illustrating the two situations. The highest occupied molecular orbital (HOMO) for the adsorbing molecule is depicted in the figure, with the ionization energy of the level indicated by \( I \).

(i) Electropositive adsorbates

Figure 3.8(a) depicts the situation for electropositive adsorbates which donate electrons towards the surface. When the first ionization energy of the adsorbate, \( I \), is lower than the work function of the surface, electron transfer to the surface takes place; this transfer ceases when the Fermi level and the HOMO are equal. The electron transfer to
the surface results in a positive charge on the adsorbates. The resulting effective dipoles are in the opposite direction to those of the clean surface and so these counteract the double layer due to the surface itself and produce a reduction in the work function. It should be noted that for conducting surfaces such as metals, image charges are set up within the surface which enhance the dipoles due to the adsorbates.

(ii) Electronegative adsorbates
Figure 3.8(b) depicts the situation for electronegative adsorbates, where the ionization energy, $I$, of the adsorbate is greater than $\phi$. The electronegative adsorbate withdraws electron density from the surface, resulting in a negatively charged adsorbate. The dipole that is produced is in the same direction as that of the clean surface and so enhances the double layer due to the surface itself, and increases the work function. Again, for conducting surfaces, the dipole produced by the adsorbate is enhanced because of the image charge produced in the surface.
The table below illustrates some typical values for work function changes at monolayer coverages.

<table>
<thead>
<tr>
<th>Substrate/adsorbate</th>
<th>$\Delta \phi_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(111)/Na</td>
<td>-2.30</td>
</tr>
<tr>
<td>Ni(110)/Na</td>
<td>-2.00</td>
</tr>
<tr>
<td>Mo(100)/K</td>
<td>-2.00</td>
</tr>
<tr>
<td>Rh/C$_2$D$_2$</td>
<td>-1.36</td>
</tr>
<tr>
<td>Rh(111)/C$_2$H$_5$</td>
<td>-1.23</td>
</tr>
<tr>
<td>Rh(111)/CO</td>
<td>+1.05</td>
</tr>
<tr>
<td>Pd(100)/H$_2$</td>
<td>+1.20</td>
</tr>
</tbody>
</table>

The work function change is both coverage and site dependent. A typical plot of work function against coverage dependence for an electronegative adsorbate is shown in Fig. 3.9(a). The coverage dependence arises from the total amount of charge that is transferred between the adsorbate and the surface. Obviously at lower coverages, less charge is transferred.

The work function change is also found to be greater following adsorption of a known amount of adsorbate on steps, when compared to that of identical amounts of adsorbate on terrace sites. Often measurements of work function change as a function of coverage are used to provide information on the surface structure and step/defect densities as these higher energy sites tend to be populated first. Indeed, work function measurements can sometimes be calibrated to provide a method of monitoring the surface coverage, using plots such as that in Fig. 3.9(a). However, the relationship between the work function change and the surface coverage is not straightforward, because adsorbate-adsorbate interactions are also involved. For example, the initial adsorption of alkali metals onto metal surfaces produces a rapid decrease in work function as shown in Fig. 3.9(b) in line with the discussion in Section 3.1.7. The linear decrease is due to the increasing total amount of negative charge transfer with increasing coverage. At a certain coverage of alkali metal, however, the now partially positively charged adsorbates are forced closer together and repel each other. The repulsion effectively ‘depolarizes’ the adsorbate–surface dipoles and so reduces the overall charge transfer between the alkali metal and the surface. The work function therefore increases again and eventually reaches a plateau, at which point the alkali atoms have formed a metallic overlayer.

3.1.8 The Langmuir

At this point it is useful to define quantities for the amounts which are dosed onto the surface. When a surface is exposed to a gas, the dosage is usually recorded in terms of the pressure of adsorbing gas and the length of time it is present in the chamber, as these factors determine the number of molecular collisions with the surface. In Section 2.5.3 it was stated that at normal temperatures (e.g., 300 K) a reactive gas of moderate molecular mass would completely cover a surface in one second if it were at a pressure of ~ $10^{-6}$ mbar ($10^{-4}$ N m$^{-2}$) and has unit sticking probability (see Section 3.2). This can be calculated using simple gas-phase collision theory; the molecular collision rate per unit area is given by

$$ \frac{dN}{dt} = \frac{P}{(2\pi m k T)^{1/2}} $$

where $N$ is the number of molecules, $P$ the gas pressure, $m$ the molecular mass, $k$ the Boltzmann constant and $T$ the temperature. The rapid rate at which the surface is covered by reactive species illustrates why ultrahigh vacuum conditions are usually
used for single-crystal 'surface science' experiments; to clean the surface atomically and keep the surface clean for long enough to carry meaningful experiments, pressures in the range $10^{-8}$ to $10^{-10}$ mbar must be used. Equilibrium conditions obtained for experiments in this pressure regime are often very different to those obtained under the 'realistic' pressure conditions which are usually required for 'real' catalytic reactions (often several atmospheres).

The Langmuir (l) is defined as a dose arising from an exposure of $10^{-4}$ torr for one second; this is equivalent to an exposure of $10^{-3}$ torr for 10 seconds or $10^{-4}$ torr for 100 seconds. However, the Langmuir term can often be misleading as although it gives a total value for the exposure of the surface to the adsorbate gas, the total amount of adsorption is dependent on the adsorption conditions, especially in terms of pressure and temperature. A particular problem is that exposure to a fixed number of Langmuirs can give different resulting coverages for different pressures (or fluxes) of gas.

The use of the non-SI unit, the torr, is unfortunate, but is historical in origin and it continues to be widely used. The conversion is that 1 atmosphere = 760 torr = 1013.25 mbar = 1.01325 x $10^5$ N m$^{-2}$ (or Pa). Thus the conversion from torr to mbar is by multiplication by 1013.25/760 = 1.333.

### 3.2 Sticking probability

The probability that an atom or molecule is adsorbed on the surface following a single collision with the surface is called the sticking probability, $s$, defined by

$$ s = \frac{\text{rate of adsorption}}{\text{rate of bombardment}} \quad (3.14) $$

For many gas-metal systems at low coverages, $s \sim 1$, i.e. the sticking process is often very efficient. For most systems the sticking probability varies with coverage and temperature. Frequently the form of plots of $s$ against $\theta$ is that they start with an initial value, $s_0$, the initial sticking probability; as the coverage is increased $s$ gradually decreases towards zero as the adsorbate-surface and adsorbate-adsorbate interactions change. In studies of the temperature dependence of $s_0$, there are two common outcomes; either it does not vary very much with temperature for a given adsorption system or it is found to decrease with increase in temperature.

#### 3.2.1 The precursor state

The characteristic shape of sticking probability curves is generally determined by the 'accommodation' of a molecule in a weakly bound physiosorbed precursor state prior to chemisorption. The precursor model was first postulated by Kilinski in 1957. He showed that the sticking coefficient could be related to the probabilities of the chemisorption, desorption and migration of a molecule from above empty and filled chemisorption sites. Taking into account the fractional coverage adsorbed on the surface, he obtained an expression for $s$ for chemisorption where the gas molecule adsorbs on a single site on the surface:

$$ s = \frac{p_\infty(1 - \theta)}{1 - p_\infty} \quad (3.15) $$

where $p_\infty$ is the probability of chemisorption above an empty site and $p_m$ is the probability of migration of the molecule across the surface from a starting position above an empty site ($\theta$ is the fractional coverage, see eqn (3.2)). When a molecule migrates to a second site on the surface, it can once again chemisorb, desorb or migrate, just as it could from the first site.

The sum of the probabilities of these processes occurring from above an empty site must equal one, that is

$$ p_\infty + p_t + p_m = 1 \quad (3.16) $$

where $p_t$ is the probability of desorption from above an empty site. The corresponding probabilities of chemisorption, $p_\infty$, desorption, $p_t$, and migration, $p_m$, for a molecule in a filled adsorption site are

$$ p_\infty = 0 \quad \text{and} \quad p_t + p_m = 1 \quad (3.17) $$

because a molecule cannot chemisorb on a site which is already filled.

If we now consider chemisorption on a surface where the fractional coverage is $\theta$, the probability that a molecule is to be found above an occupied chemisorption site is $\theta$, while the probability that it is above an unoccupied site is $(1 - \theta)$. The probability of adsorption on the first site visited, $p_{\text{first site}}$, is therefore $p_{\text{first site}} = p_\infty(1 - \theta)$. The probability of desorption from the first site visited, $p_{\text{des.}}$, is the sum of the probabilities of desorption from above empty and filled sites, which is given by $p_{\text{des.}} = p_\infty(1 - \theta) + p_m$. Substitution of these values for $p_\infty$ and $p_t$ in eqn (3.16) gives the probability of migration from the first unfilled site visited:

$$ p_{\text{migrate.}} = 1 - p_\infty - p_t + p_m(1 - \theta) \quad (3.18) $$

At zero coverage, the initial sticking probability, $s_0$, is obtained from substituting $\theta = 0$ into eqn (3.15),

$$ s_0 = \frac{p_\infty}{1 - p_m} = \frac{p_\infty}{p_\infty + p_t} \quad (3.19) $$

Taking the ratio of eqn (3.15) to eqn (3.19) then gives

$$ \frac{s}{s_0} = \left( 1 + \frac{K}{1 - \theta} \right)^{-1} \quad (3.20) $$

where

$$ K = \frac{p_t}{p_\infty + p_t} \quad (3.21) $$

Figure 3.10a shows the expected forms of the sticking probability curves for different values of $K$. The data for 'real' adsorption systems usually correspond to curves where $K < 1$. 

When $p_\infty$ is small!
3.2.2 Temperature dependence

Both the initial sticking probability and the shape of the sticking probability versus coverage curve may be temperature dependent. This is thought to be due to the pre-equilibrium between the gas phase and the precursor state; the system is usually analysed by combining the probability approach adopted in Section 3.2.1 with the rate constant. Assuming that the probabilities of surface processes are proportional to their rates, then eqn (3.19) can be rewritten

\[ s_0 = \frac{k_d}{k_a + k_d} \]  

(3.23)

where \( k_a \) and \( k_d \) are the rate constants for chemisorption and desorption of the precursor, respectively. This can be rearranged to give

\[ \frac{k_d}{k_a} = \frac{1 - s_0}{s_0} \]  

(3.24)

Each of the rate constants can be described in terms of the usual type of exponential expressions:

\[ k_d = A_d \exp \left( \frac{-E_d}{RT} \right) \]  

and \[ k_a = A_a \exp \left( \frac{-E_a}{RT} \right) \]  

(3.25)

where \( A \) denotes the pre-exponential factor and \( E \) the activation energies for desorption (subscript d) and adsorption (subscript a). \( E \) and \( T \) have their usual meanings. These expressions can be substituted into eqn (3.24) and when natural logs are taken, the following relationship is obtained, relating the activation energy barriers to the initial sticking coefficients.

\[ \ln \left( \frac{A_d}{A_a} \right) + \left( \frac{E_a - E_d}{RT} \right) = \left( \frac{1 - s_0}{s_0} \right) \]  

(3.26)

If we make the reasonable assumption that the pre-exponential factors are rather temperature independent, we can see that the temperature dependence of the initial sticking probability is governed by the difference in activation energies of adsorption and desorption.

(i) For non-activated chemisorption \( E_a < E_d \). This means that \( s_0 \) increases, and thus \( (1 - s_0)/s_0 \) decreases, as the temperature increases.

(ii) For activated chemisorption \( E_a > E_d \), which means that \( s_0 \) decreases as the temperature increases. This situation is observed far less frequently.

Generally, the sticking probability is often found to be different for different faces of the same metal crystal; this might be because of the nature of the adsorption and precursor site(s) available on the substrate. Repulsive/attractive interactions between adjacent adsorbate atoms/molecules are also found to be of importance in some cases.

The specificity of adsorption on a certain crystal surface is clearly demonstrated by the sticking probabilities for dissociative chemisorption of molecular nitrogen on different faces of tungsten, which are shown as a function of surface coverage in Fig. 3.10b). There are two types of curve in this case. For some faces, a linear dependence
of sticking probability with coverage is observed, e.g. nitrogen on W(411) and (111). For others such as nitrogen on W(310) and (100), the initial sticking probability is reasonably independent of nitrogen coverage in the low-coverage region, and then decreases with the sigmoid shape shown. The Kislik type of model for two adjacent sites can be used to model this latter behaviour, modified to take into account a pairwise repulsion effect between adjacent adsorbed nitrogen atoms. The structure of the adsorbed layer leads to small additional modifications to the Kislik model.

3.3 Adsorption isotherms and rates

An adsorption isotherm is a plot of the equilibrium amount of a substance adsorbed (in terms of coverage or uptake) against pressure of the adsorbing substance in the gas phase, measured at constant temperature. Most adsorption systems fall into one of the five categories which are sketched in Fig. 3.11.

Measurements of these isotherms can be made using either gravimetric or volumetric techniques and it turns out that types I and II are of most interest in surface science studies.

In the type I case, the amount adsorbed increases steadily with pressure until a plateau is reached at $\theta = 1$. No further adsorption occurs at this stage. This isotherm describes 'ideal' chemisorption, where molecules chemisorb until the surface becomes saturated with adsorbate, whereupon adsorption ceases.

In the type II case, as the monolayer plateau region is approached, there is a further increase in the amount adsorbed and many layers are ultimately adsorbed. This type of isotherm is usually associated with physisorption.

Of the other three categories, type III is associated with multilayer formation from the onset, and types IV and V are associated with the formation of monolayers where there are variations of heat of adsorption with $\theta$. Category IV behaviour is of considerable interest in the study of real catalysts as it implies 'hysteresis' behaviour which means that an increase in pressure to a certain level results in a different coverage when compared to the coverage formed by decreasing the pressure to the same level. This behaviour is usually observed for evaporation and condensation in pores such as those commonly found in catalysts and arises because evaporation in a porous material is not as easy as condensation, as there is a high probability of recondensation. It follows that the shape of the hysteresis can often indicate the size and type of pore in the catalyst itself.

To return to the type I and II isotherms, which apply more appropriately to studies of the flat surface, models to describe the observed behaviour have been set up. The first, the Langmuir adsorption isotherm, describes type I behaviour, whereas the Brunauer-Emmett-Teller isotherm (BET) extends the Langmuir model to reproduce physisorption phenomena of type II.

3.3.1 The Langmuir isotherm

This is the most commonly used model for an adsorption isotherm and describes ideal chemisorption systems. It can be derived on the basis of kinetic, thermodynamic, and/or statistical mechanical models. It will be derived here in kinetic terms. The assumptions made in this model are that:

(i) adsorption occurs on specific sites and all adsorption sites are identical;
(ii) the energy for adsorption is independent of how many of the surrounding sites are occupied;
(iii) only one adsorbate occupies each site and once all the sites are occupied, adsorption ceases (i.e. a maximum of one monolayer is deposited).

It is important to realize that very few systems give rise to Langmuir-like behaviour. The first and third assumptions, which imply that only one type of site is occupied, are often wrong. LEED measurements show that there are several possible binding sites available, even on the simplest, low-indexed faces. Techniques which are used to observe adsorbates, such as those discussed later in this chapter, have often revealed that more than one of these sites can be occupied in a given adsorption system. In addition, even single-crystal surfaces contain defects/step edges and these tend to be occupied first.

The second assumption is nearly always wrong. As we have seen in Sections 3.1.4 and 3.2, the heat of adsorption and the sticking probability are almost always coverage dependent. The main influences on the heat of adsorption are the total amount of charge transfer between the adsorbate and the surface, which obviously changes with coverage, and the lateral interactions between adsorbates, which are particularly noticeable at higher coverages.