We can address the question of what happens when a molecule becomes adsorbed onto a surface at two levels; specifically we can aim to identify

1. the nature of the adsorbed species and its local adsorption geometry (i.e., its chemical structure and co-ordination to adjacent substrate atoms)
2. the overall structure of the extended adsorbate/substrate interface (i.e., the long range ordering of the surface)

The latter topic is covered in detail in Section 6.1, while this section will consider only the local adsorption geometry and adsorbate structure.

Chemisorption, by definition, involves the formation of new chemical bonds between the adsorbed species and the surface atoms of the substrate - basically the same type of bonds that are present in any molecular complex. In considering what type of species may be formed on a metal surface, therefore, it is important not to abandon chemical common sense and, if in doubt, to look for inspiration at the structures of known metal-organic complexes.

**Chemisorption of Hydrogen and Halogens**

**Hydrogen (H₂)**

In the H₂ molecule, the valence electrons are all involved in the H-H σ-bond and there are no additional electrons which may interact with the substrate atoms. Consequently, chemisorption of hydrogen on metals is almost invariably a dissociative process in which the H-H bond is broken, thereby permitting the hydrogen atoms to independently interact with the substrate (see Section 2.4 for a description of the energetics of this process). The adsorbed species in this instance therefore are hydrogen atoms.

The exact nature of the adsorbed hydrogen atom complex is generally difficult to determine experimentally, and the very small size of the hydrogen atom does mean that migration of hydrogen from the interface into sub-surface layers of the substrate can occur with relative ease on some metals (e.g. Pd, rare earth metals).

The possibility of molecular H₂ chemisorption at low temperatures cannot be entirely excluded, however, as demonstrated by the discovery of molecular hydrogen transition metal compounds, such as W(η²-H₂)(CO)3(PPr₃)₂, in which both atoms of the hydrogen molecule are coordinated to a single metal centre.

**Halogens (F₂, Cl₂, Br₂ etc.)**

Halogens also chemisorb in a dissociative fashion to give adsorbed halogen atoms. The reasons for this are fairly clear - in principle a halogen molecule could act as a Lewis base and bind to the surface without breakage of the X-X bond, in practice the lone pairs are strongly held by the highly electronegative halogen atom so any such interaction would be very weak and the thermodynamics lie very heavily in favour of dissociative adsorption [ i.e. D(X-X) + D(M-X) << 2 D(M-X) ]. Clearly the kinetic barrier to dissociation must also be low or non-existent for the dissociative adsorption to occur readily.

Another way of looking at the interaction of a halogen molecule with a metal surface is as follows: the significant
difference in electronegativity between a typical metal and halogen is such that substantial electron transfer from the metal to halogen is favoured. If a halogen molecule is interacting with a metal surface then this transferred electron density will enter the $\sigma^*$ antibonding orbital of the molecule, thereby weakening the X-X bond. At the same time the build-up of negative charge on the halogen atoms enhances the strength of the metal-halogen interaction. The net result of these two effects when taken to their limit is that the halogen molecule dissociates and the halogen atoms interact with the metal with a strong ionic contribution to the bonding.

Halogen atoms tend to occupy high co-ordination sites on the surface - for example, the 3-fold hollow site on $fcc$ (111) surfaces (A) and the 4-fold hollow site on $fcc$(100) surfaces (B).

This behavior is typical of atomic adsorbates which almost invariably endeavor to maximize their co-ordination and hence prefer to occupy the highest-available co-ordination site on the surface. As a result of the electron transfer from the metal substrate to the halogen atoms, each adsorbed atom is associated with a significant *surface dipole*.

Cross-section

One consequence of this is that there are repulsive (dipole-dipole) interactions between the adsorbed atoms, which are especially evident at higher surface coverages and which can lead to a substantial reduction in the enthalpy of adsorption at specific coverages (if these coverages mark a watershed, above which the atoms are forced to occupy sites which are much closer together).

Another feature of the halogen adsorption chemistry of some metals is the transition from an adsorbed surface layer to surface compound formation at high gas exposures.

Chemisorption of Nitrogen and Oxygen

Oxygen

Oxygen is an example of a molecule which usually adsorb dissociatively, but are also found to adsorb molecularly on
some metals (e.g. Ag, Pt). In those cases where both types of adsorption are observed it is the dissociative process that corresponds to the higher adsorption enthalpy.

As noted above, in the molecular adsorption state the interaction between the molecule and the surface is relatively weak. Molecules aligned such that the internuclear axis is parallel to the surface plane may bond to a single metal atom of the surface via both

1. \( \sigma \)-donor interaction, in which the charge transfer is from the occupied molecular \( \pi \)-bonding molecular orbital of the molecule into vacant orbitals of \( \sigma \)-symmetry on the metal (i.e. \( M \leftarrow O_2 \)), and

2. \( \pi \)-acceptor interaction, in which an occupied metal \( d \)-orbital of the correct symmetry overlaps with empty \( \pi^* \) orbitals of the molecule and the charge transfer is from the surface to the molecule (i.e. \( M \rightarrow O_2 \)).

Although the interaction of the molecule with the surface is generally weak, one might expect that there might be a substantial barrier to dissociation due to the high strength (and high dissociation enthalpy) of the O=O bond. Nevertheless on most metal surfaces, dissociation of oxygen is observed to be facile which is related to the manner in which the interaction with the surface can mitigate the high intrinsic bond energy (see \textit{Section 2.4}) and thereby facilitate dissociation.

Once formed, oxygen atoms are strongly bound to the surface and, as noted previously, will tend to occupy the highest available co-ordination site. The strength of the interaction between adsorbate and substrate is such that the adjacent metal atoms are often seen to undergo significant displacements from the equilibrium positions that they occupy on the clean metal surface. This displacement may simply lead to a distortion of the substrate surface in the immediate vicinity of the adsorbed atom (so that, for example, the adjacent metal atoms are drawn in towards the oxygen and the metal-oxygen bond distance is reduced) or to a more extended surface reconstruction (see \textit{Section 1.6}).

Dissociative oxygen adsorption is frequently irreversible - rather than simply leading to desorption, heating of an adsorbed oxygen overlayer often results in either the gradual removal of oxygen from the surface by diffusion into the bulk of the substrate (e.g. Si(111) or Cu(111)) or to the formation of a surface oxide compound. Even at ambient temperatures, extended oxygen exposure often leads to the nucleation of a surface oxide. Depending on the reactivity of the metal concerned, further exposure at low temperatures may result either in a progressive conversion of the bulk material to oxide or the oxidation process may effectively stop after the formation of a passivating surface oxide film of a specific thickness (e.g. Al).

\textit{Nitrogen}

The interaction of nitrogen with metal surfaces shows many of the same characteristics as those described above for oxygen. However, in general \( N_2 \) is less susceptible to dissociation as a result of the lower M-N bond strength and the substantial kinetic barrier associated with breaking the \( N≡N \) triple bond.

\textit{Chemisorption of Carbon Monoxide}

Depending upon the metal surface, carbon monoxide may adsorb either in a molecular form or in a dissociative fashion - in some cases both states coexist on particular surface planes and over specific ranges of temperature.
1. On the reactive surfaces of metals from the left-hand side of the periodic table (e.g. Na, Ca, Ti, rare earth metals) the adsorption is almost invariably dissociative, leading to the formation of adsorbed carbon and oxygen atoms (and thereafter to the formation of surface oxide and oxy-carbide compounds).

2. By contrast, on surfaces of the metals from the right hand side of the d-block (e.g. Cu, Ag) the interaction is predominantly molecular; the strength of interaction between the CO molecule and the metal is also much weaker, so the M-CO bond may be readily broken and the CO desorbed from the surface by raising the surface temperature without inducing any dissociation of the molecule.

3. For the majority of the transition metals, however, the nature of the adsorption (dissociative v.'s molecular) is very sensitive to the surface temperature and surface structure (e.g. the Miller index plane, and the presence of any lower co-ordination sites such as step sites and defects).

Molecularly chemisorbed CO has been found to bond in various ways to single crystal metal surfaces - analogous to its behaviour in isolated metal carbonyl complexes.

Whilst the above structural diagrams amply demonstrate the inadequacies of a simple valence bond description of the bonding of molecules to surface, they do to an extent also illustrate one of its features and strengths - namely that a given element, in this case carbon, tends to have a specific valence. Consequently, as the number of metal atoms to which the carbon is co-ordinated increases, so there is a corresponding reduction in the C-O bond order.

However, it must be emphasised that a molecule such as CO does not necessarily prefer to bind at the highest available co-ordination site. So, for example, the fact that there are 3-fold hollow sites on an fcc(111) surface does not mean that CO will necessarily adopt this site - the preferred site may still be a terminal or 2-fold bridging site, and the site or site(s) which is(are) occupied may change with either surface coverage or temperature. The energy difference between the various adsorption sites available for molecular CO chemisorption appears therefore to be very small. A description of the nature of the bonding in a terminal CO-metal complex, in terms of a simple molecular orbital model, is given in Section 5.4.

Chemisorption of Ammonia and other Group V/VI Hydrides

Ammonia has lone pairs available for bonding on the central nitrogen atom and may bond without dissociation to a single
metal atom of a surface, acting as a Lewis base, to give a pseudo-tetrahedral co-ordination for the nitrogen atom.

\[
\begin{align*}
\text{H} & \quad \text{N} & \quad \text{H} \\
& \quad \quad \downarrow \\
& \quad \quad \text{M}
\end{align*}
\]

Alternatively, progressive dehydrogenation may occur to give surface NH\textsubscript{x} (x = 2, 1, 0) species and adsorbed hydrogen atoms, i.e.

\[
\text{NH}_3 \rightarrow \text{NH}_2(\text{ads}) + \text{H(ads)} \rightarrow \text{NH(ads)} + 2 \text{H(ads)} \rightarrow \text{N(ads)} + 3 \text{H(ads)}
\]

As the number of hydrogens bonded to the nitrogen atom is reduced, the adsorbed species will tend to move into a higher co-ordination site on the surface (thereby tending to maintain the valence of nitrogen).

Decomposition fragments of ammonia on an fcc(111) surface. (Picture adapted from the BALSAC Picture Gallery by K. Hermann, Fritz-Haber-Institut, Berlin)

Other Group V and Group VI hydrides (e.g. PH\textsubscript{3}, H\textsubscript{2}O, H\textsubscript{2}S) exhibit similar adsorption characteristics to ammonia.

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**Chemisorption of Unsaturated Hydrocarbons**

Unsaturated hydrocarbons (alkenes, alkynes, aromatic molecules etc.) all tend to interact fairly strongly with metal atom surfaces. At low temperatures (and on less reactive metal surfaces) the adsorption may be molecular, albeit perhaps with some distortion of bond angles around the carbon atom.

Ethene, for example, may bond to give both a π-complex (A) or a di-σ adsorption complex (B):

\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C} \quad \text{H} \\
& \quad \quad \downarrow \\
& \quad \quad \text{M}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{C} - \text{C} - \text{H} \\
& \quad \quad \downarrow \\
& \quad \quad \text{M} \\
\text{H} & \quad \text{C} - \text{C} - \text{H} \\
& \quad \quad \downarrow \\
& \quad \quad \text{M}
\end{align*}
\]

(A) Chemisorbed (B) Ethene
Further examples: models of chemisorbed ethene and ethyne on Cu(111)

As the temperature is raised, or even at low temperatures on more reactive surfaces (in particular those that bind hydrogen strongly), a stepwise dehydrogenation may occur. One particularly stable surface intermediate found in the dehydrogenation of ethene is the ethylidyne complex, whose formation also involves H-atom transfer between the carbon atoms.

![Ethylidyne](image)

*Ethylidyne: this adsorbate preferentially occupies a 3-fold hollow site to give pseudo-tetrahedral co-ordination for the carbon atom.*

The ultimate product of complete dehydrogenation, and the loss of molecular hydrogen by desorption, is usually either carbidic or graphitic surface carbon.

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