Dynamic SIMS is used as one of the major methods of quality control in the semiconductor industry, where some of the wafers being produced on the production line are measured for purity and accuracy of levels of doping.

An example of a static SIMS result is shown in Fig. 3.48(a) for the surface of a polyvinyl chloride (PVC) sample. Figure 3.48(b) shows the effect of beam damage on the surface by a beam of xenon ions. The large number and mass distribution of the fragments evolved show how complex SIMS spectra can be and indicate the vast amount of information which is contained in them.

4

Surface reactions and reactivity

4.1 Reactions

Following adsorption, as we have seen in Section 3.5 it is possible for an adsorbate to undergo a rearrangement, to fragment on the surface or to simply be desorbed in its original molecular form. It is also possible for the adsorbate to react with another species which is either co-adsorbed on the surface or in the gas phase. As we have seen in Chapter 1, it is this reactivity which is makes surfaces and reactions on or by them of such great importance in everyday life. In fact, one of the major motivations for studying surface reactions has been to apply our knowledge to the field of catalysis. A useful working definition of a catalyst is a substance which increases the rate of a chemical reaction without being consumed and much of the work described will be set in the context of catalysis.

In the chapter we will explore the mechanisms of surface reactions, discussing single molecular species and reactions involving more than one. The product formed and the nature of its adsorption is also of importance because this can limit the use of certain catalysts. For instance, it may bind very effectively to the surface and prove difficult to remove. Studies of catalysts tend to explore their macroscopic properties. For example, how efficient is the catalyst? How stable? How robust? How durable? In surface science studies we concentrate on the microscopic aspects of the heterogeneous reaction. For example, how does the catalyst work? What is the adsorption process and what is the nature of the adsorbate on the surface? From the previous chapter it is clear that in order to answer some of these important questions, the same techniques used to study adsorption can also be applied successfully to the study of surface reactions and to the detection of reaction intermediates.

One difficulty in relating surface science measurements to those in catalysis is that real catalysts work under considerably higher pressure conditions than it is possible to measure with surface science tools. For example, an atypical catalysed process operates at well over an atmosphere in pressure while typical surface science experiments can only be carried out in vacua better than 10^-6 mbau. This means that there is a pressure difference of 9-10 orders of magnitude between the two, which may well result in different behaviour. This gap is beginning to close, however, as technology begins to allow us to use high-pressure cells for adsorption and to develop techniques that use photons as the probe species. These act in a complementary manner to charged particles but do not require high vacua. In fact, IR techniques have been applied very
4.2 Transition state theory

For a reaction in the gas phase or on the surface where

\[ A + B \rightarrow C \]  

(4.1)

the rate can be found from the general expression

\[ \text{Rate} = k_e C_A^x C_B^y \]  

(4.2)

where \( C \) denotes the concentrations of the components \( A \) and \( B \), \( x \) and \( y \) are the experimentally determined orders of reaction in \( A \) and \( B \), respectively. \( k_e \) is the rate coefficient which is related to an activation energy \( E^* \) and pre-exponential factor \( A \) by:

\[ k_e = A \exp \left( \frac{-E^*}{RT} \right) \]  

(4.3)

If the reaction is a single-step one, the rate would be proportional to \( C_A C_B \), that is with the values of \( x = y = 1 \). However, the reaction normally proceeds in a series of elementary steps, in which case the observed rate equation depends on all the steps up to the slowest rate-determining one. Thus, for surface reactions the exponents can be non-integral, or even negative when one adsorbate is strongly adsorbed and excludes another.

When comparing the homogeneous process in the gas phase to the heterogeneous process involving the surface, it is found that the rate is increased for the heterogeneous process, either because \( A \) is larger or, more commonly, because the surface enables \( E^* \) to be smaller or even zero. \( E^* \) is usually reduced because the surface provides a different pathway by which the reaction can proceed. It should be noted that the surface has no effect on the position of the equilibrium, which depends entirely on the enthalpy and entropy of the overall reaction.

Figure 4.1 shows the potential energy curve illustrating the energetics involved when using transition state theory to describe how the reaction proceeds. In the homogeneous process, the reactants have a substantial activation energy barrier \( E_{\text{hom}} \). However, once they reach the transition state by overcoming this, the final product is formed rapidly.

For the comparable heterogeneous process, the reactants initially overcome the small activation energy barrier for adsorption \( E_a \) and are adsorbed on the surface. In order for the reaction to proceed, the adsorbed reactants then have to overcome the activation energy barrier \( E_{\text{lat}} \) to form the heterogeneous transition state, which normally requires considerably less energy than formation of the homogeneous transition state (i.e., \( E_{\text{lat}} < E_{\text{hom}} \)). The products are then adsorbed on the surface and they desorb once they have overcome \( E_d \), the activation energy barrier for desorption of the product species. The total energy difference between the initial reactants and final products in the gas phase is the same for both homogeneous and heterogeneous processes, which is why the equilibrium position is the same for each. Making the assumption that the rate-determining step is excitation to the transition state, the reaction proceeds faster on the surface because of the relative sizes of \( E_{\text{lat}} \) and \( E_{\text{hom}} \). It should be noted from eqn (4.3) that in cases where the rate of a surface reaction is temperature dependent, the rate depends on both the value of \( E_{\text{lat}} \) and the temperature \( T \).

It is not too surprising to note that the overall reaction rate for the surface reaction is dependent on the surface area of the catalyst. This means that in order for it to be
worthwhile to carry out a heterogeneous reaction rather than the homogeneous one, there must be both sufficient surface available and a sufficient reduction in the activation energy barrier. To illustrate this we will look at the bimolecular reaction in eqn (4.1). The rate of the homogeneous reaction is given by

$$R_{\text{homo}} = C_A C_B A \exp \left[ \frac{-E_{\text{homo}}}{RT} \right] = C_A C_B \frac{kT}{h} \frac{\phi_{\text{homo}}}{\phi_A \phi_B} \exp \left[ \frac{-E_{\text{homo}}}{RT} \right]$$  (4.4)

where $C_A$ and $C_B$ refer to the gas-phase concentrations of adsorbates A and B per unit volume. The pre-exponential factor, $A$, is determined from the partition functions, $\phi_A$ and $\phi_B$, which sum the contributions of translational, electronic, vibrational, and rotational states in statistical thermodynamics; $\phi_A$ and $\phi_B$ are the partition functions of components A and B and $\phi_{\text{homo}}$ is the partition function for the homogeneous transition state, where one degree of freedom (motion along the reaction coordinate) is factored out. ($k$ is the Boltzmann constant, $T$ the temperature and $h$ the Planck constant.)

For the heterogeneous reaction, a similar expression is obtained:

$$R_{\text{hetero}} = C_A C_B C_S \frac{kT}{h} \frac{\phi_{\text{het}}}{\phi_A \phi_B} \exp \left[ \frac{-E_{\text{het}}}{RT} \right]$$  (4.5)

$C_A$ and $C_S$ refer to concentrations per unit area of adsorbed species, but for our purposes we will assume that the surface species are in concentrations which are directly proportional to the gas-phase concentration, thus $C_A = C_S$. Making the further assumption that reaction takes place only between adjacent adsorbed A and B molecules, the term $C_S$, the concentration of adjacent pairs of surface sites, must be introduced. This is true if both A and B are adsorbed on the surface (the so-called Langmuir-Hinshelwood reaction mechanism, see Section 4.5.1). $\phi_{\text{het}}$ is the partition function for the heterogeneous transition state. In order to assess the difference in activation energies required to make the heterogeneous process viable, we take the ratio of the two rates:

$$\frac{R_{\text{hetero}}}{R_{\text{homo}}} = C_S \frac{\phi_{\text{het}}}{\phi_{\text{homo}}} \exp \left[ \frac{\Delta E}{RT} \right]$$  (4.6)

where

$$\Delta E = E_{\text{homo}} - E_{\text{het}}$$  (4.7)

$\phi_{\text{het}}$ includes translational motion whereas $\phi_{\text{homo}}$ does not, because translational motion is lost on the surface. Since translational energies are considerably larger than vibrational, rotational, etc., the following substitution can be made:

$$\frac{\phi_{\text{het}}}{\phi_{\text{homo}}} \approx \frac{1}{\phi_{\text{trans}}} \approx \frac{1}{7 \times 10^{16}}$$  (4.8)

where $\phi_{\text{trans}}$ is the partition function for the translations. A value of $\sim 7 \times 10^{16}$ is typical for a fairly light gas molecule such as $D_2$ at room temperature (for our purposes, this was calculated for a molecule confined in a 100 cm$^3$ vessel). The value of $\phi_{\text{trans}}$ indicates that $7 \times 10^{16}$ quantum states are accessible. Substitution for the ratios of the partition functions given in eqn (4.8) into eqn (4.6) then gives

$$\frac{R_{\text{hetero}}}{R_{\text{homo}}} = C_S \frac{1}{\phi_{\text{trans}}} \exp \left[ \frac{\Delta E}{RT} \right]$$  (4.9)

As we have seen in Chapter 2, a surface has approximately $10^{14}$-10$^{15}$ sites cm$^{-2}$. Taking $5 \times 10^{14}$ as a typical value of $C_S$, we find that to obtain equal rates, $\Delta E = 69.8$ kJ mol$^{-1}$ for a total surface area of 1 cm$^2$, at 300 K. In other words, under these conditions the activation energy barrier for the heterogeneous process must be at least 69.8 kJ mol$^{-1}$ lower than that of the homogeneous process for the heterogeneous process to be viable. However, it should be noted that considerably smaller reductions than this are usually sufficient because real working catalysts have very large surface areas (often hundreds or thousands of square centimetres).

### 4.3 Selectivity

In the previous section we saw that a heterogeneous process can accelerate a reaction. Another important feature of surface reactions is that they can provide a degree of selectivity in the products, by making accessible different possible reaction pathways. Reactions can be sequential, that is of the form

$$A \rightarrow B \rightarrow C$$  (4.10)

or parallel, where different products are produced on the same surface.

$$A \rightarrow B$$
$$A \rightarrow C$$  (4.11)

In the former case, catalysts can be chosen to select the reaction product B rather than C or vice versa. An example of a sequential reaction is the oxidation of hydrocarbons such as ethene. The reaction is given in eqn (4.12) and a schematic potential energy curve and the most significant states formed are given in Fig. 4.2.

$$C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O \rightarrow \text{H}_2O + \text{CO}_2$$  (4.12)

For the real process there are number of intermediate steps, but the key role of the catalyst is in reducing the activation energy barrier of the first step ($C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O$) to almost zero. The catalyst has no effect on the second major step in the reaction, that is from the $C_2H_4O$ intermediate to the final states. Water and carbon dioxide are the most thermodynamically stable products, but the catalysed reaction can be used to selectively enhance the less stable products by speeding up their formation rate relative to their destruction rate.

The role of the substrate material (or materials, in the case of real catalysts) is vital in determining the products formed. A prime example of this is in the reactions of...
Fig. 4.2 A schematic potential energy curve for the oxidation of ethene. (Solid lines indicate the homogeneous process and dashed lines show the heterogeneous process.)

synthesis gas, which is a mixture of carbon monoxide and hydrogen. It is usually made by passing steam over coal. Figure 4.3 shows the products resulting from passing synthesis gas over several different metals.

The reaction of CO and hydrogen on copper produces methanol. This reactivity results from the nature of the interaction of CO with copper. The d orbitals of copper are full and so the interaction with CO is weak; too weak, in fact, to enable the C=O bond to be broken. The steps which are likely to be involved in the process are shown in Fig. 4.4. Initially it is thought that CO and hydrogen adsorb onto the copper surface. H then binds sequentially to the carbon atoms, first forming adsorbed HCO, then CH₃O, and finally methoxide, CH₂O. In the final step of the process, an OH species is formed and the methanol is then desorbed.

\[
\begin{align*}
C + H₂O &\rightarrow CO + H₂ & \text{Methanol synthesis} \\
C + H₂O &\rightarrow CH₄ + H₂O & \text{Methanation} \\
C₃H₂O &\rightarrow CH₄ + H₂O & \text{Fischer-Tropsch} \\
\end{align*}
\]

Fig. 4.3 The reaction scheme for the synthesis gas reaction over different metals.

Fig. 4.4 Schematic diagram of the generally accepted mechanism for methanol synthesis from synthesis gas over a copper-based catalyst.

Methanol synthesis over copper-based catalysts is of such great industrial importance that a massive amount of research has been conducted on it over the past twenty or more years, using a variety of surface science techniques. It should be noted that in the real catalytic process, the gaseous mixture which is passed over the supported copper catalyst contains not only carbon monoxide and hydrogen but also carbon dioxide. The experimental evidence suggests that the mechanism that occurs over the real catalyst involves hydrogenation of the carbon dioxide to formate, followed by stepwise hydrogenation to methanol. This process is more energetically favourable than the process involving only CO and hydrogen.

The transition metals Ni, Co and Fe are more reactive than Cu because their partially filled d orbitals are able to take part in bonding to the adsorbates. These partially filled d-bands enable the metals to break the C=O bond in carbon monoxide. (The C=O bond is one of the strongest bonds known; the bond energy is ~ 105 kJ mol⁻¹.) Under appropriate conditions, particularly in terms of temperature, each of these metals is found to completely dissociate the CO, forming adsorbed C and O on the surface. (For example, nickel can only dissociate CO above room temperature.)

The generally accepted mechanism for methanation by a nickel-based catalyst is shown in Fig. 4.5. Following the initial dissociative chemisorption, adsorbed hydrogen atoms bind sequentially with the carbon atom until a CH₃ adsorbate species is formed. Binding to a further hydrogen atom results in the formation of methane which is readily desorbed to the gas phase. The Fischer-Tropsch synthesis of hydrocarbons over Co- or Fe-based catalysts is found to proceed similarly. Polymerization of the CH₃ species to form heavier hydrocarbon fragments or the surface is found to be favoured on these surfaces.
4.4 Reactivity

The reactivity of a substrate depends on the electronic and geometric structures of the materials from which it is composed. These structures depend not only on the properties of the specific elements present but also on how these elements interact with each other (see Chapter 3). Two key factors governing the reactivity are, therefore, the nature of the elements in the substrate and the crystal faces which are exposed. Volcano curves can be used to compare the reactivities of different transition metals and are discussed in Section 4.4.1. In Chapter 3 we saw that the structure of a substrate can have a considerable effect on adsorption; in Section 4.4.2 the effect of substrate structure on the reactivity will be discussed.

4.4.1 Volcano curves

From the surface reactions described in Section 4.3, it is apparent that there is a link between the nature of the chemisorption of a species on the surface and its reactivity. If chemisorption is 'weak' then low coverages of adsorbate will be formed and the surface reactivity (or catalytic activity) will be low. As the heat of adsorption increases, bonding to the surface becomes stronger and the uptake increases, giving higher surface coverages and reduced energies of activation. Thus, the catalytic activity will be greater. At the other extreme, if an adsorbate interacts too strongly with the surface, the latter will quickly become covered by adsorbed species and the surface-adsorbate system may then be too stable to decompose or react further. The catalytic activity will, in this case, be low.

The catalytic activity of a surface for a given reaction can be plotted against the atomic number (or a similar suitable parameter such as the d-band occupancy) to show how the activity changes with substrate across the periodic table. Looking at the example of the Fischer-Tropsch synthesis of hydrocarbons which was given in Section 4.3, Fig. 4.6 shows a schematic plot of the catalytic activity against atomic number. It is clear that the catalytic activity is low for Sc on the left-hand side of the periodic table. Activity increases to a maximum at Co and then decreases again towards copper on the right-hand side of the period. This type of plot is typically known as a 'Balandin volcano plot'.

A comparison of the volcano plot with the nature of the chemisorption of CO shows a distinct correlation. For substrates from Sc to Mn the chemisorption of CO is too strong to allow this reaction to proceed. However, adsorption on Fe, Co and Ni gives a sufficiently reactive CO adsorbate to enable it to react once chemisorbed. In terms of the Fischer-Tropsch synthesis the catalytic activity is greater on Fe and Co compared to that on Ni. While the conversion of hydrocarbons does take place on Ni with similar activity to that on Fe, it turns out that the preferred product on Ni is methane itself. On copper, as we have seen, the surface is insufficiently reactive to crack the CO and so the catalytic activity for hydrocarbon synthesis is very low.

Similar volcano plots are found for most catalytic processes. Obviously they peak at different metals depending on the process under investigation. For example, for methane synthesis from synthesis gas, the volcano plot is strongly peaked at Ni and for methanol synthesis the volcano plot is peaked at copper. These volcano curves can therefore be used to select the most suitable metal for carrying out a desired surface reaction. Generally they correlate the strength of chemisorption with the reactivity. The peak usually occurs at some region of intermediate strength of chemisorption, with reactivity being low at the extremes where very weak and very strong adsorption is found.

The relative catalytic activities for different metals can be characterized by the temperature at which a given rate of reaction is attained (lower temperatures representing higher activities) or by the rate coefficient (k) for the reaction at a given temperature (a high rate coefficient representing high activity). The use of k is not altogether satisfactory however. From eqn (4.3) we know that k involves both A and E, and these vary with substrate. If both vary together (i.e. both vary in the same direction) on changing substrate, they counteract each other (the so-called 'compensation effect', where the change in A compensates for the change in E). This is, in practice, a common finding and may give a misleading view of the relative catalytic activities of the surfaces.

A more satisfactory method of quantifying the volcano plot is to combine the Langmuir isotherm (given in eqn (3.33) in Section 3.3.1) with transition state theory (Section 4.2) to investigate the rates of reaction across the periodic table. The starting
Point is to use the rate expression for a single adsorbing species. The heterogeneous reaction rate \( R_{\text{hetero}} \) is given by

\[
R_{\text{hetero}} = k_{\text{het}} \theta
\]

(4.13)

where \( \theta \) is the coverage of adsorbate and \( k_{\text{het}} \) the rate coefficient. The right-hand and left-hand sides of the volcano plot are then dealt with separately.

### 4.4.1.1 The right-hand side of the volcano plot

To look at reactions on substrates on the right-hand side of the volcano curve, use can be made of the characteristic temperatures at which a reaction on one substrate equals the rate on another. For weak chemisorption on substrates on the right-hand side of the volcano plot, the heat of adsorption, \( \Delta H_{\text{ads}} \), is low and so is \( \theta \) (see eqn (3.32) in Section 3.3.1) is small. Thus \( b' \ll 1 \). The expression for coverage \( \theta \) can then be written in terms of \( b' \) and \( b \):

\[
\theta = \frac{b'}{\text{const}} \exp \left( \frac{-\Delta H_{\text{ads}}}{RT} \right)
\]

(4.14)

where 'const' collects together all the constant terms in \( b \) as given in eqn (3.32). The rate coefficient \( k_{\text{het}} \) is given by

\[
k_{\text{het}} = A_{\text{het}} \exp \left( \frac{-E_{\text{het}}}{RT} \right)
\]

(4.15)

Feeding eqns (4.14) and (4.15) into eqn (4.13) results in

\[
R_{\text{het}} = A_{\text{het}} \frac{b'}{\text{const}} \exp \left( \frac{-\Delta H_{\text{ads}} - E_{\text{het}}}{RT} \right)
\]

(4.16)

To compare two substrates \( X \) and \( Y \), we can take ratios of expression (4.16), as it applies to the two substrates. This gives the two temperatures \( T_X \) and \( T_Y \), at which their rates \( R_X \) and \( R_Y \) are equalized.

Because the exponential terms normally dominate, the pre-exponential factors can be ignored. When \( R_X = R_Y \), the two exponential terms are equal and so

\[
\frac{\Delta H_X + E_{\text{net}}}{T_X} = \frac{\Delta H_Y + E_{\text{net}}}{T_Y}
\]

(4.17)

where the heat of adsorption \( \Delta H \) and activation energy \( E_{\text{net}} \) for \( X \) and \( Y \) are indicated by subscripts. What we want to know is how the heat of adsorption plus activation energy barrier for substrate \( X \) varies compared to that on substrate \( Y \). An example of this would be on going from a copper catalyst (X) to a nickel one (Y) when considering the synthesis gas reactions. (CO is more strongly bound on nickel.) Rearranging eqn (4.17) and for convenience making the assumption that \( E_{\text{net}} \approx E_{\text{net}} \) enable us to simplify the expression to eqn (4.18). Note that this is a very likely situation but adopting it allows us to draw some reasonable comparisons between substrates.

\[
\Delta H_X + E_{\text{net}} = \frac{\Delta \Delta H_{\text{ads}} T_X}{\Delta T}
\]

(4.18)

where \( \Delta T = T_Y - T_X \) and \( \Delta \Delta H_{\text{ads}} = \Delta H_Y - \Delta H_X \).

Equation (4.18) can thus be used to compare adjacent substrates on the right-hand side of the volcano curve. For simple single-step processes, the left side of eqn (4.18) is always positive because although heats of adsorption are negative, the activation energy barrier is always positive and larger than the heat of adsorption. For the right side of eqn (4.18), an increase in adsorbate interaction with the surface going from \( X \) to \( Y \) (or \( Cu \) to \( Ni \) in our example) gives a negative value of \( \Delta \Delta H_{\text{ads}} \), which means that \( \Delta T \) must also be negative. Thus \( T_X > T_Y \) or; in our example, \( T_{Cu} > T_{Ni} \), which is observed. In addition, the linear relationship between \( \Delta \Delta H_{\text{ads}} \) and \( \Delta T \) is apparent and can be seen in the slope on the right-hand side of the volcano curves.

It should be noted that in complex multistep processes, the overall activation energy barrier may be smaller than the heat of adsorption because of changes in energy affecting the bottom of the potential energy curve.

### 4.4.1.2 The left-hand side of the volcano plot

On the left-hand side of the volcano plot, \( \Delta H_{\text{ads}} \) is large because chemisorption is strong. This means that \( b'' \ll 1 \) and so \( \theta \approx 1 \). Thus, eqn (4.13) reduces to

\[
R_{\text{hetero}} = k_{\text{het}}
\]

(4.19)

and the reaction is therefore of zero order. Considering eqn (4.15), this implies that the activation energy for the reaction \( E_{\text{net}} \) is the only energy term which affects the rate and that changing \( \Delta H_{\text{ads}} \) does not obvious. This is not what is observed and we must look more closely at \( E_{\text{net}} \).

In this case, it is thought that changes in the energy with which the molecule binds to the surface affect the bottom of the potential energy curve rather than they affect the transition state. It is thus assumed that the heterogeneous activation energy, \( E_{\text{net}} \), is dependent on both the heat of adsorption and the energy difference between the gas-phase reactants and the transition state, \( \Delta E_{\text{net}} \). \( \Delta E_{\text{net}} \) is shown in Fig. 4.1 and is this energy which is thought to be insensitive to the strength of the chemisorption. \( R_{\text{net}} \) is given by

\[
E_{\text{net}} = -\Delta H_{\text{ads}} + \Delta E_{\text{net}}
\]

(4.20)

and the rate can be given by

\[
R_{\text{hetero}} = k_{\text{het}} = A_{\text{het}} \exp \left( \frac{-\Delta H_{\text{ads}} + \Delta E_{\text{net}}}{RT} \right)
\]

(4.21)

It should be noted that for the right-hand side of eqn (4.21) there is a roughly linear relationship between \( \Delta H_{\text{ads}} \) and the temperature. Bearing this in mind, if we consider the implications of eqn (4.21) it is apparent that as the heat of adsorption decreases, so the reaction goes faster. This expression therefore satisfactorily models the behaviour observed on the left-hand side of the volcano curve, in the region of strong chemisorption.
4.4.1.3 Two-reactant systems

For a situation in which there are two adsorbates A and B on the surface, as in eqn (4.1), the rate expression is expected to take a general form

$$R = k_2 \theta_A \theta_B$$

(4.22)

Volcano plots can be produced for the reaction of A and B. The strengths and relative strengths of chemisorption of both components dictate how efficient the reaction process will be. If one of the components is too strongly adsorbed in comparison to the other, for example if A is much more strongly bound than B, then A will quickly produce a coverage of $\theta_B \approx 1$. There will consequently be no sites available for B to adsorb and the reaction will not proceed. If it does proceed, with difficulty, the rate will depend on $\theta_B^1$.

4.4.2 Structure sensitivity

One area in which surface science studies have usefully been applied to heterogeneous catalytic processes is in the investigation of reaction rates as a function of the surface structure. Studies of the reaction rate have been carried out on a range of flat (low-indexed, stepped and kinked surfaces. Typical reactions studied include aromatization (e.g. n-hexane to benzene and n-heptane to methyl benzene) and cyclization (e.g. ethyne to benzene). It is found that these reactions proceed much faster on the (111) faces of fcc metals such as platinum compared to their rates on (100) faces. For the aromatization reactions it has been found that the hexagonal (111) face is between three and seven times more active than the square-based (100) mesh. This activity difference is due to the type and nature of the adsorption site(s) available for both the reactants and the products formed. A hexagonal substrate mesh is particularly suitable for reactions where benzene is formed because the substrate offers a "template" for the binding of the appropriate atomic dimensions and geometry. In other words, benzene "fits" neatly into the hexagonal structure of the Pt(111) surface.

Further work on aromatization on Pt has shown that even faster rates are obtained for reactions on stepped and kinked surfaces, with maximum rates being achieved on stepped surfaces with hexagonal terraces about five atoms wide. The role of steps and kinks is not yet understood but it is clear that they often provide regions of considerable reactivity. The difference in their chemical behaviour compared to that of the terraces is due to their very different local atomic structural environments which cause them to have very different electronic charge densities.

The surface structure (both electronic and geometric) can be modified by adsorption of another species to alter the reactivity or to improve efficiency of a given reaction. For example if potassium is adsorbed on a metal such as Fe, it donates electrons to the iron which increases the negative charge available for bonding to adsorbates. This is borne out by the observation that CO is more strongly bound on the K-modified surface (its CO stretching frequency is lower) than on the clean surface. K is often used as an electronic promoter, with its most important use, as K₂O, on the Fe-based ammonia synthesis catalyst.

Structure modifiers are also widely used, usually to block sites which are too reactive. For example, when carrying out the hydrogenolysis of organic molecules on Pt, kink and step sites often produce undesirable low molecular weight products. It is found that H₂S reacts on Pt to form adsorbed S. The S is much more strongly bound to the steps and kinks than to the terrace sites. Controlled exposure to H₂S can therefore be used to block these sites. Such selective poisoning of the kinks and steps leaves the terraced sites available to produce the desired higher molecular weight products.

4.5 Reaction mechanisms

It is important that we have some idea of the mechanisms by which surface reactions proceed and much of the early insight into these came from the study of their kinetics. There are two generally accepted models for surface reactions, namely the Langmuir-Hinshelwood (LH) and the Rideal-Eley (RE) mechanisms. Observations of how changes in pressure and temperature affect the reaction rate can be used to distinguish between the two mechanisms and these are described in detail in Sections 4.5.1 and 4.5.2. It should be noted that these simple kinetic studies can be ambiguous to some degree (see Sections 4.5.3-4.6). Rather more sophisticated models and methods are usually needed to properly elucidate a given surface reaction mechanism. These limitations are discussed further in Section 4.5.3.

4.5.1 The Langmuir-Hinshelwood (LH) mechanism

In this reaction scheme all reactants involved in the reaction are adsorbed on the surface prior to reacting. When using simple kinetics to study this mechanism, several assumptions are made:

(i) the reaction at the surface is the rate-determining step of the overall reaction;
(ii) the Langmuir isotherm can be applied to all gases involved in the reaction (and so its assumptions also apply—see Chapter 3, Section 3.3.1);
(iii) adsorbates compete for the same surface sites.

The mechanism can be discussed for a number of different situations.

4.5.1.1 Unimolecular surface reaction with immediate desorption of the product

In this case a single species, A, is adsorbed and either undergoes a rearrangement or decomposition to form a product B which is immediately desorbed, that is

$$A_{\text{ads}} \rightarrow B_{\text{gas}}$$

(4.23)

Substitution for $\theta_A$ from the Langmuir isotherm in Section 3.3.1, eqn (3.33), gives an expression for the rate of reaction R:

$$R = k_\text{tot} \theta_A = \frac{\theta_A \beta_A P_A}{1 + \theta_A \beta_A}$$

(4.24)