

## 2.6: The Desorption Process

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. As the temperature of the substrate is increased, however, there will come a point at which the thermal energy of the adsorbed species is such that one of several things may occur:

1. a molecular species may decompose to yield either gas phase products or other surface species.
2. an atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid.
3. the species may desorb from the surface and return into the gas phase.

The last of these options is the desorption process. In the absence of decomposition the desorbing species will generally be the same as that originally adsorbed but this is not necessarily always the case.

(An example where it is not is found in the adsorption of some alkali metals on metallic substrates exhibiting a high work function where, at low coverages, the desorbing species is the alkali metal ion as opposed to the neutral atom. Other examples would include certain isomerization reactions.)

### Desorption Kinetics

The rate of desorption,  $R_{des}$ , of an adsorbate from a surface can be expressed in the general form:

$$R_{des} = kN^x \quad (2.6.1)$$

with

- $x$  - kinetic order of desorption
- $k$  - rate constant for the desorption process
- $N$  - surface concentration of adsorbed species

The order of desorption can usually be predicted because we are concerned with an [elementary step](#) of a "reaction": specifically,

#### I. Atomic or Simple Molecular Desorption



- will usually be a first order process (i.e.  $x = 1$ ). Examples include ...

- The desorption of copper atoms from a tungsten surface



- the desorption of CO molecules from a copper surface



#### II. Recombinative Molecular Desorption



- will usually be a second order process (i.e.  $x = 2$ ). Examples include:

- desorption of O atoms as  $O_2$  from a Pt surface



- desorption of H atoms as  $H_2$  from a Ni surface



The rate constant for the desorption process may be expressed in an [Arrhenius form](#),

$$k_{des} = A \exp(-E_a^{des}/RT) \quad (2.6.9)$$

with

- $E_a^{des}$  is the activation energy for desorption, and
- $A$  is the pre-exponential factor; this can also be considered to be the "attempt frequency",  $\nu$ , at overcoming the barrier to desorption.

This then gives the following general expression for the rate of desorption

$$R_{des} = -\frac{dN}{dt} = \nu N^x \exp(-E_a^{des}/RT) \quad (2.6.10)$$

In the particular case of simple molecular adsorption, the pre-exponential/frequency factor ( $\nu$ ) may also be equated with the frequency of vibration of the bond between the molecule and substrate; this is because every time this bond is stretched during the course of a vibrational cycle can be considered an attempt to break the bond and hence an attempt at desorption.

## Surface Residence Times

One property of an adsorbed molecule that is intimately related to the desorption kinetics is the *surface residence time* - this is the average time that a molecule will spend on the surface under a given set of conditions (in particular, for a specified surface temperature) before it desorbs into the gas phase.

For a first order process such as the desorption step of a molecularly adsorbed species:



the average time ( $\tau$ ) prior to the process occurring is given by:

$$\tau = \frac{1}{k_1} \quad (2.6.12)$$

where  $k_1$  is the first order rate constant (no proof of this will be given here).

From equation 3 with  $x = 1$ , we know that

$$k_1 = \nu \exp(-E_a^{des}/RT) \quad (2.6.13)$$

and if we also substitute for  $E_a^{des}$  using the approximate relation  $E_a^{des} \approx -\Delta H_{ads}$  discussed in [Section 2.4](#), then we get the following expression for the surface residence time

$$\tau = \tau_o \exp(-\Delta H_{ads}/RT) \quad (2.6.14)$$

with

- $\tau_o$  corresponds to the period of vibration  $\approx 1/\nu$  of the bond between the adsorbed molecule and substrate and is frequently taken to be about  $10^{-13}$  s .

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