2.3: Kinetics of Adsorption

The rate of adsorption, R_{ads}, of a molecule onto a surface can be expressed in the same manner as any kinetic process. For example, when it is expressed in terms of the partial pressure of the molecule in the gas phase above the surface:

$$R_{ads} = k' P^x \tag{2.3.1}$$

where:

- x - kinetic order
- k' - rate constant
- P - partial pressure

If the rate constant is then expressed in an Arrhenius form, then we obtain a kinetic equation of the form:

$$R_{ads} = A e^{-E_a/RT} P^x \tag{2.3.2}$$

where E_a is the activation energy for adsorption and A the pre-exponential (frequency) factor. It is much more informative, however, to consider the factors controlling this process at the molecular level. The rate of adsorption is governed by (1) the rate of arrival of molecules at the surface and (2) the proportion of incident molecules which undergo adsorption. Hence, we can express the rate of adsorption (per unit area of surface, i.e., molecules m^{-2} s^{-1}) as a product of the incident molecular flux, F, and a sticking probability, S.

$$R_{ads} = S F \tag{2.3.3}$$

The sticking probability varies from 0 (never sticking) to 1 (always sticking). The flux (in molecules m^{-2} $s^{-1)}$ of incident molecules is given by the **Hertz-Knudsen equation**

$$F = \frac{P}{\sqrt{2\pi m k T}} \tag{2.3.4}$$

where

- P - gas pressure [N m^{-2}]
- m - mass of one molecule [kg]
- T - temperature [K]

The sticking probability is clearly a property of the adsorbate / substrate system under consideration but must lie in the range 0 < S < 1; it may depend upon various factors - foremost amongst these being the existing coverage of adsorbed species (θ) and the presence of any activation barrier to adsorption. In general,therefore

$$S = f(\theta) e^{-E_a/RT} \tag{2.3.5}$$

where, once again, E_a is the activation energy for adsorption and $f(\theta)$ is some, as yet undetermined, function of the existing surface coverage of adsorbed species. Combining the equations for S and F yields the following expression for the rate of adsorption:

$$R = \frac{f(\theta) P}{\sqrt{2\pi m k T}} e^{-E_a/RT} \tag{2.3.6}$$

1. Equation 2.3.6 indicates that the rate of adsorption is expected to be first order with regard to the partial pressure of the molecule in the gas phase above the surface.
2. It should be recognized that the activation energy for adsorption may itself be dependent upon the surface coverage, i.e. $E_a = E(\theta)$.
3. If it is further assumed that the sticking probability is directly proportional to the concentration of vacant surface sites (which would be a reasonable first approximation for non-dissociative adsorption) then $f(\theta)$ is proportional to $(1 - \theta)$, where, in this instance, θ is the fraction of sites which are occupied (i.e. the Langmuir definition of surface coverage).

For a discussion of some of the factors which determine the magnitude of the activation energy of adsorption you should see Section 2.4 which looks at the typical PE curve associated with various types of adsorption process.

Estimating Surface Coverages arising as a result of Gas Exposure

If a surface is initially clean and it is then exposed to a gas pressure under conditions where the rate of desorption is very slow, then the coverage of adsorbed molecules may initially be estimated simply by consideration of the kinetics of adsorption. As noted above, the rate of adsorption is given by Equation 2.3.3, which can be written in term of a derivative

$$\frac{dN_{ads}}{dt} = S\,F \tag{2.3.7}$$

where N_{ads} is the number of adsorbed species per unit area of surface.

Equation 2.3.7 must be integrated to obtain an expression for N_{ads}, since the sticking probability is coverage (and hence also time) dependent. However, if it is assumed that the sticking probability is essentially constant (which may be a reasonable approximation for relatively low coverages), then this integration simply yields:

$$N_{ads} = SFt \tag{2.3.8}$$