

3.1: Introduction

Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid.

As with all chemical equilibria, the position of equilibrium will depend upon a number of factors:

1. The relative stabilities of the adsorbed and gas phase species involved
2. The temperature of the system (both the gas and surface, although these are normally the same)
3. The pressure of the gas above the surface

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

The Langmuir isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. There are many other types of isotherm (Temkin, Freundlich ...) which differ in one or more of the assumptions made in deriving the expression for the surface coverage; in particular, on how they treat the surface coverage dependence of the enthalpy of adsorption. Whilst the Langmuir isotherm is one of the simplest, it still provides a useful insight into the pressure dependence of the extent of surface adsorption.

Note: Surface Coverage & the Langmuir Isotherm

When considering adsorption isotherms it is conventional to adopt a definition of surface coverage (θ) which defines the maximum (saturation) surface coverage of a particular adsorbate on a given surface always to be unity, i.e. $\theta_{max} = 1$. This way of defining the surface coverage differs from that usually adopted in surface science where the more common practice is to equate θ with the ratio of adsorbate species to surface substrate atoms (which leads to saturation coverages which are almost invariably less than unity).

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