

## 3.2: Langmuir Isotherm - derivation from equilibrium considerations

We may derive the Langmuir isotherm by treating the adsorption process as we would any other equilibrium process - except in this case the equilibrium is between the gas phase molecules ( $M$ ), together with vacant surface sites, and the species adsorbed on the surface. Thus, for a non-dissociative (molecular) adsorption process, we consider the adsorption to be represented by the following chemical equation:



where:

- $S - *$  represents a vacant surface site

### Assumption 1

In writing Equation 3.2.1 we are making an inherent assumption that there are a fixed number of localized surface sites present on the surface. This is the first major assumption of the Langmuir isotherm.

We may now define an equilibrium constant ( $K$ ) in terms of the concentrations of "reactants" and "products"

$$K = \frac{[S - M]}{[S - *][M]} \quad (3.2.2)$$

We may also note that:

- $[S - M]$  is proportional to the surface coverage of adsorbed molecules, i.e. proportional to  $\theta$
- $[S - *]$  is proportional to the number of vacant sites, i.e. proportional to  $(1-\theta)$
- $[M]$  is proportional to the pressure of gas,  $P$

Hence, it is also possible to define another equilibrium constant,  $b$ , as given below:

$$b = \frac{\theta}{(1 - \theta)P} \quad (3.2.3)$$

Rearrangement then gives the following expression for the surface coverage

$$\theta = \frac{bP}{1 + bP} \quad (3.2.4)$$

which is the usual form of expressing the Langmuir Isotherm. As with all chemical reactions, the equilibrium constant,  $b$ , is both temperature-dependent and related to the Gibbs free energy and hence to the enthalpy change for the process.

### Assumption 2

$b$  is only a constant (independent of  $\theta$ ) if the enthalpy of adsorption is independent of coverage. This is the second major assumption of the Langmuir Isotherm.

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