

3.3: Langmuir Isotherm from a Kinetics Consideration

The equilibrium that may exist between gas adsorbed on a surface and molecules in the gas phase is a dynamic state, i.e. **the equilibrium represents a state in which the rate of adsorption of molecules onto the surface is exactly counterbalanced by the rate of desorption of molecules back into the gas phase**. It should therefore be possible to derive an isotherm for the adsorption process simply by considering and equating the rates for these two processes.

Expressions for the rate of adsorption and rate of desorption have been derived in Sections 2.3 & 2.6 respectively: specifically,

$$R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi mkT}} \exp(-E_a^{ads}/RT) \quad (3.3.1)$$

$$R_{des} = v f'(\theta) \exp(-E_a^{ads}/RT) \quad (3.3.2)$$

Equating these two rates yields an equation of the form:

$$\frac{P f(\theta)}{f'(\theta)} = C(T) \quad (3.3.3)$$

where θ is the fraction of sites occupied at equilibrium and the terms $f(\theta)$ and $f'(\theta)$ contain the pre-exponential surface coverage dependence of the rates of adsorption and desorption respectively and all other factors have been taken over to the right hand side to give a temperature-dependent "constant" characteristic of this particular adsorption process, $C(T)$. We now need to make certain simplifying assumptions. The first is one of the key assumptions of the Langmuir isotherm.

Note: Assumption 1

Adsorption takes place only at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.

Let us initially further restrict our consideration to a simple case of **reversible molecular adsorption**, i.e.



where

- S_{-} represents a vacant surface site and
- $S-M$ the adsorption complex.

Under these circumstances it is reasonable to assume coverage dependencies for rates of the two processes of the form:

- **Adsorption** (forward reaction in Equation 3.3.4):

$$f(\theta) = c(1 - \theta) \quad (3.3.5)$$

i.e. proportional to the fraction of sites that are unoccupied.

- **Desorption** (reverse reaction in Equation 3.3.4):

$$f'(\theta) = c'\theta \quad (3.3.6)$$

i.e. proportional to the fraction of sites which are occupied by adsorbed molecules.

Note

These coverage dependencies in Equations 3.3.5 and 3.3.6 are exactly what would be predicted by noting that the forward and reverse processes are elementary reaction steps, in which case it follows from standard chemical kinetic theory that

- The forward adsorption process will exhibit kinetics having a first order dependence on the concentration of vacant surface sites and first order dependence on the concentration of gas particles (proportional to pressure).
- The reverse desorption process will exhibit kinetics having a first order dependence on the concentration of adsorbed molecules.

Substitution of Equations 3.3.5 and 3.3.6 into Equation 3.3.3 yields:

$$\frac{P(1-\theta)}{\theta} = B(T) \quad (3.3.7)$$

where

$$B(T) = \left(\frac{c'}{c}\right) C(T). \quad (3.3.8)$$

After rearrangement this gives the *Langmuir Isotherm* expression for the surface coverage

$$\theta = \frac{bP}{1+bP} \quad (3.3.9)$$

where $b = 1/B(T)$ is a function of temperature and contains an exponential term of the form

$$b \propto \exp[(E_a^{des} - E_a^{ads})/RT] = \exp[-\Delta H_{ads}/RT] \quad (3.3.10)$$

with

$$\Delta H_{ads} = E_a^{des} - E_a^{ads}. \quad (3.3.11)$$

Note: Assumption 2

b can be regarded as a **constant** with respect to coverage only if the enthalpy of adsorption is itself **independent** of coverage; this is the second major assumption of the Langmuir Isotherm.

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