Adsorption and desorption

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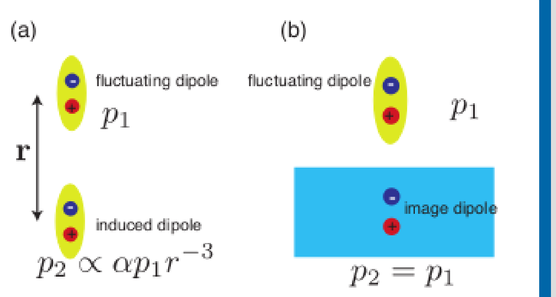
Physisorption

Principle



Math

Normal vdW:

$$E_1 \propto r^{-3}$$
$$p_2 \propto \alpha p_1 r^{-3}$$
$$U \propto p_2 E_1 \propto r^{-6}$$

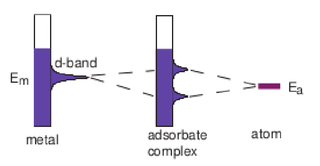
In physisorption the second dipole is an image charge:

$$p_2 = p_1$$
$$U \propto p_2 E_1 \propto r^{-3}$$

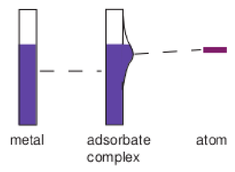
The range is several Å, the energyrange is 10 meV to 100 meV

Chemisorption

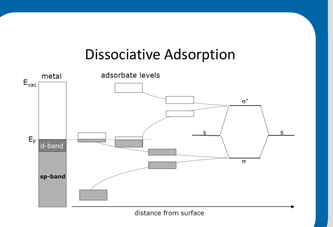
d band scheme



metal scheme



dissociative adsorption



Newns–Anderson model math

$$\psi = c_m \psi_m + c_a \psi_a$$

where m is the metal and a is the adsorbate. The system then has the energies:

$$E_m = \int \psi_m^* H \psi_m \, d\mathbf{r}$$
$$E_a = \int \psi_a^* H \psi_a \, d\mathbf{r}$$
$$-V = \int \psi_a^* H \psi_m \, d\mathbf{r} = \int \psi_m^* H \psi_a \, d\mathbf{r}$$

And the overlap

$$S = \int \psi_m^* \psi_a \, d\mathbf{r}$$
$$H\psi = E\psi$$
$$\int \psi_a^* H \psi = -c_m V + c_a E_a = E_a(S c_m + c_a)$$
$$\int \psi_m^* H \psi = -c_a V + c_m E_m = E_m(S c_a + c_m)$$

Or in matrix form:

$$\begin{bmatrix} E - E_a & V - ES \\ V - SE & E - E_m \end{bmatrix} = 0$$

For simplicity $S = 0$ can be assumed

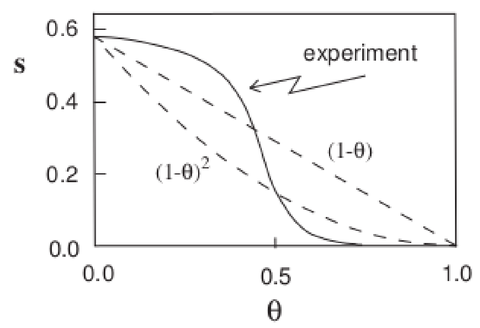
$$E_{1,2} = \frac{E_a + E_m}{2} \pm \sqrt{\left(\frac{E_a - E_m}{2}\right)^2 + V^2}$$
$$E_{1,2} = \bar{E} \pm \Delta$$
$$c_a = c_m \frac{E_1 - E_m}{V} \qquad \text{For the lower state}$$
$$c_a = c_m \frac{E_2 - E_m}{V} \qquad \text{For the upper state}$$

Kinetics — The Langmuir model

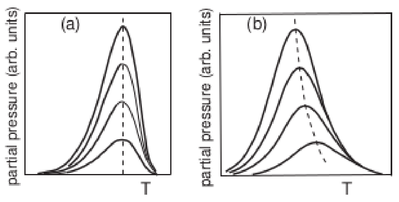
Adsorption

Desorption

Experimental results



TDS experiment



Langmuir math

$$\frac{d\Theta}{dt} = S\frac{dN}{dt} = S\frac{P}{\sqrt{2\pi M k_b T}}$$

where, N is the number of sites (N_0 would be the number of sites on a clean surface), S is the sticking coefficient:

$$S = c(1-\Theta)^n e^{\frac{E_a}{k_b T}} = S_0(1-\Theta)^n$$

S_0 is the sticking coefficient on a clean surface. c is the fraction of incoming molecules adsorbed on a clean surface. $(1-\Theta)^n$ takes care of the fact that the adsorption probability changes with coverage. The ^{n} describes the order; at zeroth order new adsorbants can sit on top of old adsorbants, at first order the adsorption is associative, at second order the adsorption is dissociative. The last factor is the energy requirement for the process, in total this gives:

$$\frac{d\Theta}{dt} = \frac{P}{\sqrt{2\pi M k_b T}} c(1-\Theta)^n e^{\frac{E_a}{k_b T}}$$

c, E_a and n are unknown.

This model is often too simple, as it doesn't mind physisorption. Physisorption can act as a precursor to chemisorption and thus making binding more likely at lower coverages and less likely at higher coverages.

Langmuir desorption and Clausius–Claperyon formulæ

$$T = T_0 + \beta t$$
$$-\frac{d\Theta}{dt} \propto P_{\text{partial}}$$
$$-\frac{d\Theta}{dt} = \nu \Theta^n e^{-\frac{E_d}{k_b T}}$$

maximum at:

$$\frac{d^2\Theta}{dt^2} = 0$$
$$\Downarrow \qquad n = 1$$
$$E_d = kT_m \ln\left(\frac{kT_m^2 \nu}{E_d \beta}\right)$$

$$\nu \Theta^n e^{-\frac{E_d}{k_b T}} = \frac{P}{\sqrt{2\pi M k_b T}} c(1-\Theta)^n e^{\frac{E_a}{k_b T}}$$

Or:

$$P = \frac{\sqrt{2\pi M k_b T}}{c} \nu_n \left(\frac{\Theta}{1-\Theta}\right)^n e^{-\frac{E_d - E_a}{k_b T}}$$
$$E_d - E_a = -k \left(\frac{\partial \ln(P)}{\partial \frac{1}{T}}\right)\Bigg|_\Theta$$