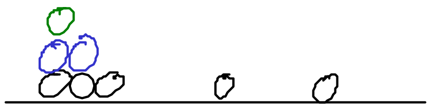
BET — Multilagen Adsorption



1. Lage — 2 Lage — 3. Lage

1. Lage Bindungsenergie ε_a

2 und höhere Lagen ε_m

Annahme: $\varepsilon_m \ll \varepsilon_a$

Gesucht: $\Theta(p_a) \quad (= \Theta(\varepsilon, \mu(p_a)) = \Theta(\varepsilon, p_a))$

$$Z_G = \sum_{n}^{\infty} z_n \, e^{\beta \mu n}$$

$$Z_n = (Z_1) Z^{n-1} \qquad n \geq 2$$

$$\underbrace{Z_1 = \exp(\beta \varepsilon_a)}_{\text{1. Lage}} \qquad \underbrace{Z = \exp(\beta \varepsilon_m)}_{\text{über 1. Lage}}$$

$$Z_G = 1 + \exp(\beta \mu) Z_m \sum_{n=0}^{\infty} Z^n \exp(\beta n \mu)$$

$$Z_G = \frac{1 - (Z - Z_1)\exp(\beta \mu)}{1 - Z \exp(\beta \mu)}$$

$$\Theta = \frac{\langle n \rangle}{N} \rightarrow \sum_{n=0}^{\infty} n \underbrace{P(n)}_{\text{Wahrscheinlichkeit für } n \text{ Teilchen}}$$

$$\Theta = \frac{1}{Z_G} \sum_{n=0}^{\infty} n Z_n \exp(\beta \mu n)$$

$$\Theta = \frac{1}{Z_G} Z_1 \exp(\beta \mu) \underbrace{\sum_{n=0}^{\infty} n Z_n \exp(\beta (n-1) \mu)}_{A}$$

$$A = \frac{1}{(1 - Z\exp(\beta\mu))^2}$$

$$\sum_{n=1}^{\infty} n x^{n-1} = \frac{1}{(1-x)^2}$$

$$\Theta = \frac{1}{Z_G} \frac{Z_1 \exp(\beta\mu)}{(1 - Z\exp(\beta\mu))^2} = \frac{Z_1 \exp(\beta\mu)}{(1-(Z-Z_1)\exp(\beta\mu))(1-Z\exp(\beta\mu))}$$

$$= \frac{\exp(\beta(\varepsilon_a + \mu))}{1 + \exp(\beta(2\varepsilon_m + \mu)) + \exp(\beta(\varepsilon_m + \varepsilon_a + \mu))}$$

Ich

Tafel $\left[1 - (\exp(\beta\varepsilon_m) - \exp(\beta\varepsilon_A))\exp(\beta\mu)\right]\left[1 - \exp(\beta(\varepsilon_m + \mu))\right]$

Grenzfall Langmuir

$\varepsilon_m = 0$?

$\varepsilon_m \longrightarrow \infty \quad \Rightarrow \quad Z = 0 \qquad \Theta(p) \Rightarrow$ Langm.

$$\Theta = \frac{Z_1 \exp(\beta\mu)}{1 + Z_1\exp(\beta\mu)} \qquad Z_1 = \exp(\beta\varepsilon_a)$$

$$\Theta = \frac{\exp[\beta(\varepsilon_a + \mu_a)]}{1 + \exp[\beta(\varepsilon_a + \mu_a)]}$$

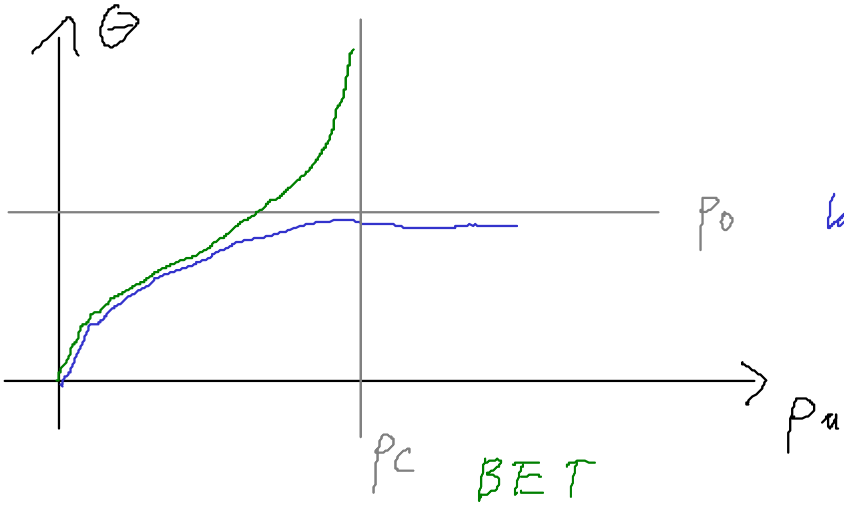
vgl $\Theta = \dfrac{p_a}{p_a + p_0(T)} = \dfrac{\exp(\beta(\varepsilon_a + \mu))}{1 + \exp(\beta(\varepsilon_a + \mu))}$

$$\frac{p_0(T)}{p_a} = \exp[-\beta(\varepsilon_a + \mu)]$$

$$\Theta = \frac{\frac{p_a}{p_0}}{\left[1 - \exp(\beta(\varepsilon_m + \mu)) + \frac{p_a}{p_0}\right]\left[1 - \exp(\beta(\varepsilon_m + \mu))\right]}$$

BET - Isotherme

$$\Theta = \frac{p_a p_0}{\left[p_0 + p_a - p_a \exp[\beta(\varepsilon_m - \varepsilon_a)]\right]\left[p_0 - p_a \exp(\beta(\varepsilon_m - \varepsilon_a))\right]}$$



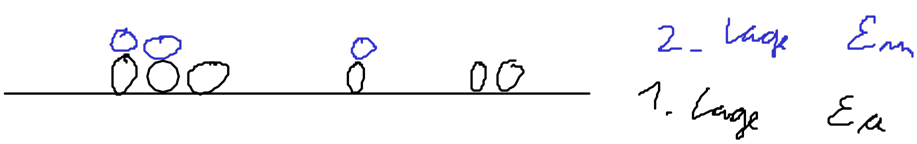
$$\Theta \longrightarrow \infty \quad \text{wenn} \quad p_a = \frac{p_0}{\exp(\beta(\varepsilon_m - \varepsilon_a))} =: p_c$$

$$p_c = p_c(T, \varepsilon_m, \varepsilon_a)$$

$$p_0(T) = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} kT \exp(-\beta \varepsilon_a)$$

$$p_c = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} kT \exp(-\beta \varepsilon_m)$$

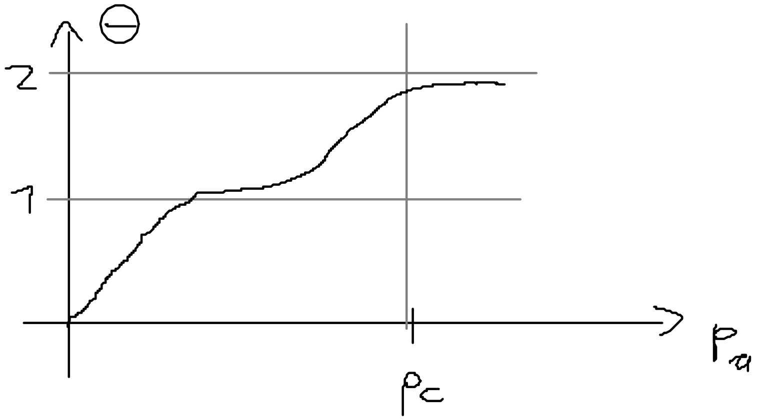
Annahme: 2 Lagen



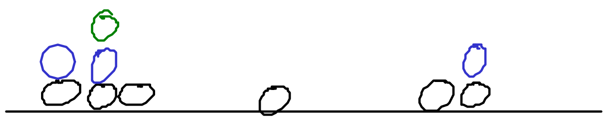
in BET: n bis 2 summieren

$$\sum_{n=0}^{\infty} \Rightarrow \sum_{n=0}^{2}$$

$$\Theta = \frac{p_a + 2\frac{p_a^2}{p_0}\exp[\beta(\varepsilon_m - \varepsilon_a)]}{p_0 + p_a + \frac{p_a^2}{p_0}\exp(\beta(\varepsilon_m - \varepsilon_a))}$$



Messung: $\Theta, p_a, T \Rightarrow \varepsilon_m$ und ε_a



gesucht $\Theta(t, p_a)$

Randbedingung $\theta(0) = 0 \qquad \theta(\infty) = \theta(p_a)$

$$R_{ads} = \frac{\sigma p_a}{\sqrt{2\pi k m T}} \left[(1 - \theta_a) + 1 \right]$$

$$R_{des} = k_1 \theta_a + k_2 \theta_m \qquad k_1 = \nu_1 \exp(-\beta \varepsilon_a) \qquad k_2 = \nu_2 \exp(-\beta \varepsilon_m)$$

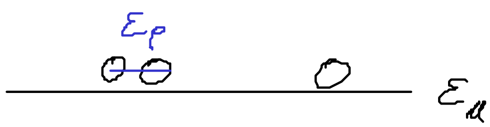
$$\Theta = \theta_a + \theta_m$$

$$\dot{\Theta} = R_{ads} - R_{des} = A_a \left[(1 - \theta_a) + 1 \right] - \nu_1 \exp(-\beta \varepsilon_a)\,\theta_a - \nu_2 (-\beta \varepsilon_m)\,\theta_m$$

↯ ? Desorption aus untere Lage wenn diese vollständig bedeckt ist ?

Adsorption in 2. Lage wenn 1. Lage leer ??

2D Gas-Modell



$E_{A-A} \neq 0$

$E_{A-A} = \mathcal{E}_p$ (Paarbindungsenergie)

N_{as} , N_{aa}

Zahl der Teilchen — Zahl der Paare

$$E = -\underbrace{N_{as}\,\mathcal{E}_a}_{\text{Langmuir}} - \underbrace{N_{aa}\,\mathcal{E}_p}_{\text{Paarbildung}}$$

$\Theta(p) \Rightarrow \mathcal{E}_a, \mathcal{E}_p$ — nur eine Lage

$$Z = \exp(\beta\, \mathcal{E}_a N_{as}) \sum_{N_{aa}} B(N_{as}, N_{aa}) \exp(\beta\, 2\, \mathcal{E}_p N_{aa})$$

$N_{aa} = \langle N_{aa} \rangle_{N_{as}}$ — Bragg-Williams-Näherung

$$\sum_{N_{aa}} B(N_{as}, N_{aa}) = C_N^{N_{as}} = \binom{N_{as}}{N}$$

$\binom{n}{k}$-Zahlen

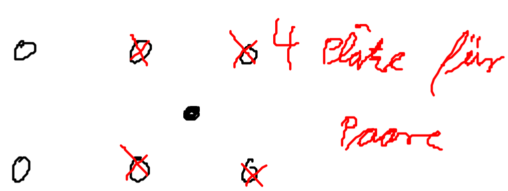
$$Z = C_N^{N_{as}} \exp\left[\beta\left(N_{as}\,\mathcal{E}_a + 2\langle N_{aa}\rangle_{N_{as}}\,\mathcal{E}_p\right)\right]$$

$$\Theta = \frac{N_{as}}{N}$$

Koordinationszahl, hier 4

$$\langle N_{aa} \rangle = \frac{1}{2} N z\, \Theta^2 \qquad \Theta \propto N_{as}$$

$$= \frac{1}{2} z \frac{N_{as}^2}{N}$$



$$\mu = -kT \frac{\partial}{\partial N} \ln(Z) \Big|_{T,N}$$

$$Z = C_N^{N_{as}} \exp\left[\beta\left(N_{as}\,\varepsilon_a + z N \Theta^2\right)\right]$$

$$\mu = kT \ln\left[\frac{\Theta}{1-\Theta}\right] - \varepsilon_A - 2z\,\Theta\,\varepsilon_p$$

Koord. Zahl

$$\mu_a = \mu_{Gas}$$

$$\mu_{Gas} = kT \ln\left(\frac{p_a}{kT}\left(\frac{h^2}{2\pi k m T}\right)^{3/2}\right)$$

$$p_a = \frac{\Theta}{1-\Theta}\, p_0(T)\, \exp\left(-\frac{2z\Theta\varepsilon_p}{kT}\right)$$

$$\frac{2z\varepsilon_p}{kT}\Theta - \ln\left(\frac{\Theta}{1-\Theta}\right) = \ln\frac{p_a}{p_0} \quad \Rightarrow \quad \Theta(p_a)$$

$$\left.\begin{matrix}\text{LEED}\\ \text{AS}\\ \text{XPS}\\ \text{TDS}\end{matrix}\right\} \Rightarrow \Theta, z \quad \text{mit} \quad \left.\begin{matrix} p_a \\ T \end{matrix}\right\} \Rightarrow \varepsilon_p, \varepsilon_a$$