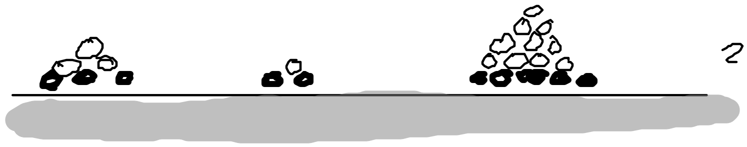
BET Multilagenadsorption



↑ 3., 2. } $\Rightarrow \varepsilon_m$

1. Lage $\Rightarrow \varepsilon_a$

$\varepsilon_m \ll \varepsilon_a$

1. Lage: Chemisorption

2. → … Lage: Physisorption

- Zu Zeitpunkt t n Teilchen an Oberfläche
- Zustandssumme

$$\Xi = \sum_{n=0}^{\infty} Z_n \exp\left[\frac{1}{kT} n \mu_a\right]$$

$$Z_n = Z^n = Z_1 Z^{n-1} \quad n \geq 2$$

$$\underbrace{Z_1 = \exp\left[\frac{1}{kT}\varepsilon_a\right]}_{\text{1. Lage}} \quad \underbrace{Z = \exp\left[\frac{1}{kT}\varepsilon_m\right]}_{\text{weitere Lage}}$$

$$\Xi = 1 + \exp\left[\frac{1}{kT}\mu_a\right] Z_1 \sum_{n=0}^{\infty} Z^n \exp\left[\frac{1}{kT}\mu_a n\right]$$

$$\boxed{\Xi = \frac{1-(Z-Z_1)\exp\left[\frac{1}{kT}\mu_a\right]}{1 - Z\exp\left[\frac{1}{kT}\mu_a\right]}}$$

- mittlere Zahl der Teilchen auf Oberfläche

$$\Theta = \frac{\langle n \rangle}{N} \Rightarrow \sum_{n=0}^{\infty} n P(n)$$

$$\Theta = \frac{1}{\Xi} \sum_{n=0}^{\infty} n Z_n \exp\left[\frac{1}{kT} n \mu_a\right]$$

$$= \frac{1}{\Xi} Z_1 \exp\left[\frac{1}{kT}\mu_a\right] \underbrace{\sum_{n=0}^{\infty} n Z_n \exp\left[\frac{1}{kT}(n-1)\mu_a\right]}_{A}$$

$$A = \frac{1}{\left(1 - Z\exp\left[\frac{1}{kT}\mu_a\right]\right)^2}$$

- $$\sum_{n=0}^{\infty} n x^{n-1} = \frac{1}{(1-x)^2}$$ <u>hier</u>: $x = Z \exp\left[\frac{1}{kT}\mu_a\right]$

$$\Rightarrow \Theta = \frac{1}{\Xi} \frac{Z_1 \exp\left[\frac{1}{kT}\mu_a\right]}{\left(1 - Z\exp\left[\frac{1}{kT}\mu_a\right]\right)^2}$$

$$= \frac{Z_1 \exp\left[\frac{1}{kT}\mu_a\right]\left(1 - Z\exp\left[\frac{1}{kT}\mu_a\right]\right)}{\left(1 - Z\exp\left[\frac{1}{kT}\mu_a\right]\right)^2\left(1-(Z-Z_1)\exp\left[\frac{1}{kT}\mu_a\right]\right)}$$

$$= \frac{\exp[\frac{1}{kT}(\mu_a+\varepsilon_a)]}{(1-\exp[\frac{1}{kT}\varepsilon_m]-\exp[\frac{1}{kT}(\varepsilon_a+\mu_a)])(1-\exp[\frac{1}{kT}(\varepsilon_m+\mu_a)])}$$

- vernachlässige physisorption:

$\varepsilon_m \to \infty$, $z=0$ → $\Theta(p)$ ⇒ Langmuir

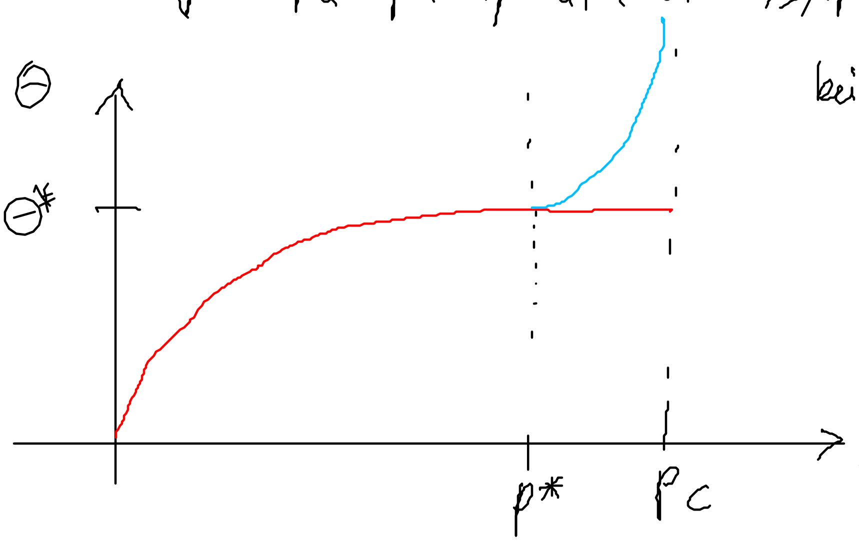
$$\Theta = \frac{z_1\exp[\frac{1}{kT}\mu_a]}{1+z_1\exp[\frac{1}{kT}\mu_a]} = \frac{\exp[\frac{1}{kT}(\mu_a+\varepsilon_a)]}{1+\exp[\frac{1}{kT}(\varepsilon_a+\mu_a)]}$$

- vgl mit $\bar{\Theta}(p_a) = \frac{p_a}{p_a+p_0(T)} = \Theta$ $\quad \frac{p_0(T)}{p_a} \doteq \exp[-\frac{1}{kT}(\varepsilon_a+\mu_a)]$

$$\Rightarrow \boxed{\Theta = \frac{\frac{p_a}{p_0(T)}}{(1-\exp[\frac{1}{kT}(\varepsilon_m+\mu_a)]+\frac{p_a}{p_0(T)})(1-\exp[\frac{1}{kT}(\varepsilon_m+\mu_a)])}}$$

BET-Isotherme

$$\Theta = \frac{p_a p_0}{(p_0+p_a-p_a\exp[\frac{1}{kT}(\varepsilon_m-\varepsilon_a)])(p_0-p_a\exp[\frac{1}{kT}(\varepsilon_m-\varepsilon_a)])}$$



bei $\Theta \to \infty$:

$$p_a = \frac{p_0(T)}{\exp[\frac{1}{kT}(\varepsilon_m-\varepsilon_a)]} = p_c$$

$$p_0(T) = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} kT\exp[-\frac{1}{kT}\varepsilon_a]$$

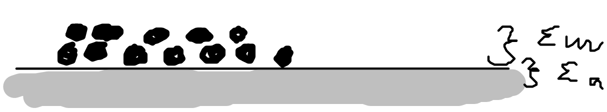
$$p_c = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} kT\exp[-\frac{1}{kT}\varepsilon_a]$$

- Gleichgewicht von R_{ads} und R_{des} temperaturabhängig
- ab einem kritischen Druck p_c ⇒ Sättigung

Bei p_a = konst ⇒ $T, \varepsilon_m, \varepsilon_A$

2 Lagen Modell

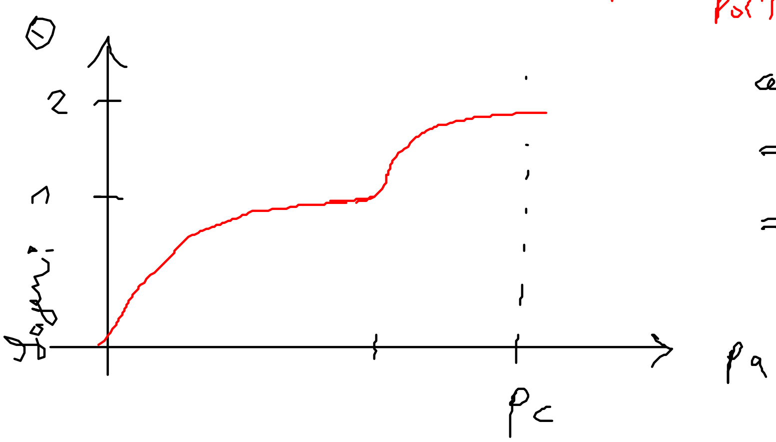
keine weiteren Schichten möglich



$\varepsilon_m(n=3)=0$

⇒ BET bei $n \leq 2$ $\sum_{n=0}^{\infty}$ ⇒ $[\ _0\ ][\ _1\ ][\ _2\ ]$

Aufgabe: $$\Theta = \frac{p_a + 2 p_a^2 \exp\left[\frac{1}{kT}(\varepsilon_m - \varepsilon_a)\right]\frac{1}{p_0(T)}}{p_0 + p_a + \frac{p_a^2}{p_0(T)} \exp\left[\frac{1}{kT}(\varepsilon_m - \varepsilon_a)\right]}$$

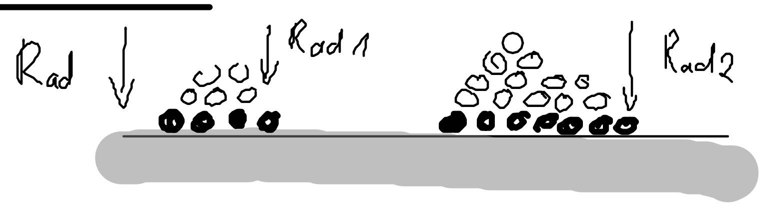


aus Experiment: T und p_a

⇒ $\varepsilon_m, \varepsilon_a$ → Mikrosystem

⇒ Spektroskopie → Θ

Kinetik des BET Modells



- gesucht $\Theta(t)$

$$\Theta(t) = \Theta_a(t) + \Theta_m(t)$$

$$R_{ad} = \frac{\sigma\, p_a}{\sqrt{2\pi k m T}}\left((1-\Theta_a(t)) + 1\right)$$

$$R_{des} = k_{des}\,\Theta_a(t) + k_{des}\,\Theta_m(t)$$

$$k_{des1} = \nu_1 \exp\left[-\frac{1}{kT}\varepsilon_a\right]$$

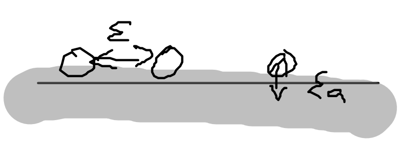
$$k_{des2} = \nu_2 \exp\left[-\frac{1}{kT}\varepsilon_m\right]$$

$$\frac{d}{dt}\Theta(t) = k_a(p)\left((1-\Theta_a(t)) + 1\right) - \nu_1 \exp\left[-\frac{1}{kT}\varepsilon_a\right]\Theta_a(t) - \nu_2 \exp\left[-\frac{1}{kT}\varepsilon_m\right]\Theta_m(t)$$

Aufgabe bis Donnerstag: $\Theta(t)$ bestimmen

2D Gas-Modell

- Erweiterung der Langmuir isotherme



berücksichtige laterale Wechselwirkung

$E_{1-1} \neq 0$ $E_{1-1} = \varepsilon$, N Plätze auf Oberfl.

- N_{aa} Zahl der Paare auf der Oberfläche
- N_{as} Zahl der einzelnen Teilchen an Oberfl.

$$\Rightarrow E = \underbrace{-N_{as}\,\varepsilon_a}_{\text{Langmuir}} - N_{aa}\,\varepsilon$$

- Zustandssumme $Z = \exp\left[\frac{1}{kT} N_{as}\,\varepsilon_a\right] \sum_{N_{aa}} B(N_{as}, N, N_{aa}) \exp\left[\frac{1}{kT} 2 N_{aa}\,\varepsilon\right]$
- Bragg-Williams-Näherung:

$$N_{aa} \approx \langle N_{aa} \rangle_{N_{as}}$$

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

$$Z = C_N^{N_{as}} \exp\left[\frac{1}{kT}\left(N_{as}\,\varepsilon_a + 2\langle N_{aa}\rangle_{N_{as}}\,\varepsilon\right)\right]$$

- $\Theta = \frac{N_{as}}{N}$ $\qquad\qquad \Theta \propto N_{as} \propto Z \cdot \Theta$

$$\langle N_{aa}\rangle_{N_{as}} = \frac{1}{2} N Z \Theta^2 = \frac{1}{2} Z \frac{N_{as}^2}{N}$$

Koordinationszahl Z der nächsten Nachbarn

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

$$Z = C_N^{N_{as}} \exp\left[\frac{1}{kT}\left(N_{as}\,\varepsilon_a + Z N \Theta^2\right)\right]$$

$$\mu = kT \ln\left(\frac{\Theta}{1-\Theta}\right) - \varepsilon_a - 2 Z \Theta \varepsilon$$

- $\mu_a = \mu_{gas}$ (ideales Gas)

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

$$p_a = \frac{\Theta}{1-\Theta} p_0(T) \exp\left[-\frac{2 Z \Theta \varepsilon}{kT}\right]$$

$$\frac{2 Z \varepsilon}{kT}\Theta - \ln\frac{\Theta}{1-\Theta} = \ln\left(\frac{p_0}{p_a}\right) \Rightarrow \Theta(p_a)$$

experimentell:

LEED
AS
XPS
TDS

} Θ, Z und $p_a, T \Rightarrow$ bestimme $\varepsilon, \varepsilon_a$