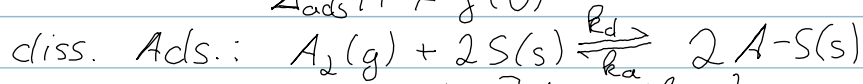


13.06.12

## Adsorptionsisotherme

Langmuir: keine Ww. ads. Moleküle

$$\Delta_{\text{ads}} H \neq f(\theta)$$



$$K_c = \frac{k_a}{k_d} = \frac{[A-S]^2}{[A_2][S]^2}$$

$$v_a = k_a [A_2] (1-\theta)^2 \sigma_0^2$$

$$v_d = k_d \theta^2 \sigma_0^2$$

im GG :  $v_a = v_d$

$$k_a [A_2] (1-\theta)^2 = k_d \theta^2$$

$$\sqrt{K_c [A_2]} (1-\theta) = \theta$$

$$\theta = \frac{\sqrt{K_c [A_2]}}{1 + \sqrt{K_c [A_2]}}$$

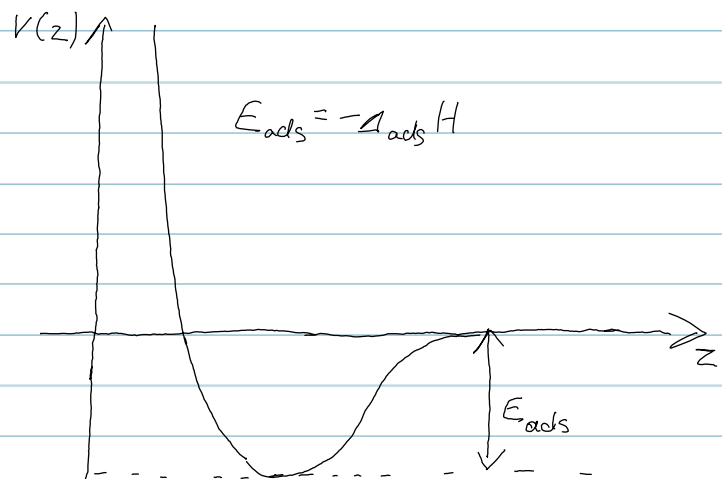
$$[A_2] = \frac{p_{A_2}}{RT}; \text{ mit } b_{A_2} = \frac{K_c}{RT}$$

$$\theta = \frac{\sqrt{b_{A_2} p_{A_2}}}{1 + \sqrt{b_{A_2} p_{A_2}}}$$

Interpretation von  $1/k_d$  als Verweilzeit

$$k_d = \frac{1}{\tau_0} e^{-\frac{E_{\text{ads}}}{RT}}$$

$$\tau = \tau_0 e^{-\frac{E_{\text{ads}}}{RT}}$$

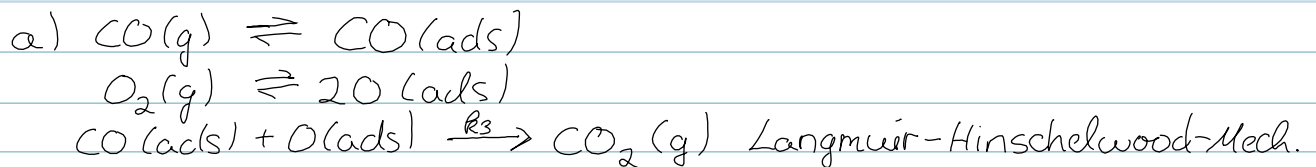


z.B. 10 ads auf Pd  
 $A_{\text{ads}}H = -146 \text{ kJ/mol}$   
 $\tau$  bei 300K, 500K?

$$\begin{aligned} \Rightarrow \tau(300\text{K}) &= 2,6 \cdot 10^{13} \text{ s} \\ \Rightarrow \tau(500\text{K}) &= 1800 \text{ s} \end{aligned} \left. \vphantom{\begin{aligned} \Rightarrow \tau(300\text{K}) \\ \Rightarrow \tau(500\text{K}) \end{aligned}} \right\} \tau \text{ stark von } T \text{ abhängig}$$

### Oberflächenreaktionen

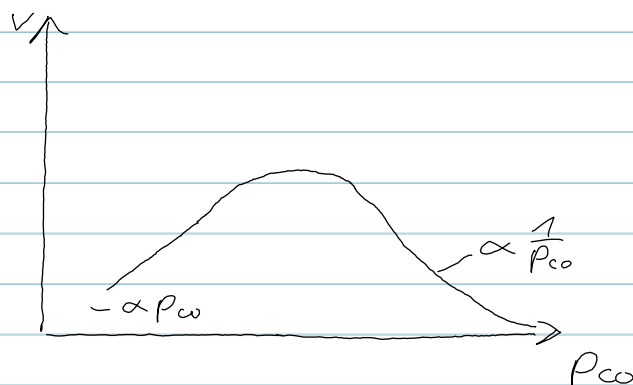
z.B. CO-Ox. auf Pt  
 $2 \text{ CO}(g) + \text{O}_2(g) \rightarrow 2 \text{ CO}_2(g)$

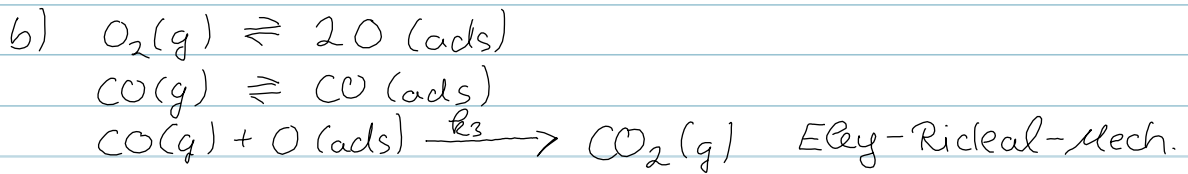


$$v = \frac{k_3 b_{\text{CO}} \sqrt{b_{\text{O}_2}} p_{\text{CO}} \sqrt{p_{\text{O}_2}}}{(1 + \sqrt{b_{\text{O}_2}} p_{\text{O}_2} + b_{\text{CO}} p_{\text{CO}})^2} \quad (\rightarrow \text{siehe ÜB 10})$$

$$p_{\text{CO}} \ll p_{\text{O}_2}: \quad v \approx \frac{k_3 b_{\text{CO}} \sqrt{b_{\text{O}_2}} p_{\text{CO}} \sqrt{p_{\text{O}_2}}}{(1 + \sqrt{b_{\text{O}_2}} p_{\text{O}_2})^2} \propto p_{\text{CO}}$$

$$p_{\text{CO}} \gg p_{\text{O}_2}: \quad v \approx \frac{k_3 b_{\text{CO}} \sqrt{b_{\text{O}_2}} p_{\text{CO}} \sqrt{p_{\text{O}_2}}}{(b_{\text{CO}} p_{\text{CO}})^2} \propto \frac{1}{p_{\text{CO}}}$$

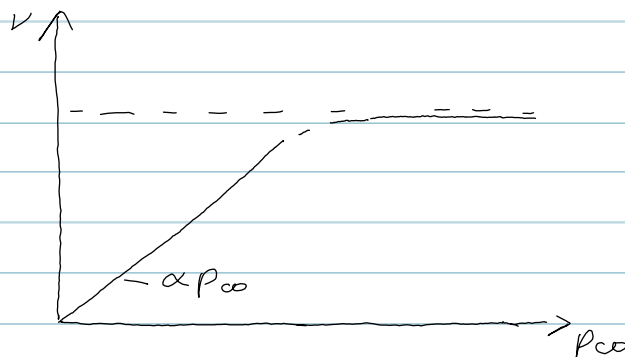




$$v = \frac{k_3 b_{CO} \sqrt{b_{O_2}} p_{CO} \sqrt{p_{O_2}}}{1 + \sqrt{b_{O_2}} p_{O_2} + b_{CO} p_{CO}}$$

$$p_{CO} \ll p_{O_2}: \quad v \approx \frac{k_3 b_{CO} \sqrt{b_{O_2}} p_{CO} \sqrt{p_{O_2}}}{1 + \sqrt{b_{O_2}} p_{O_2}} \propto p_{CO}$$

$$p_{CO} \gg p_{O_2}: \quad v \approx \frac{k_3 b_{CO} \sqrt{b_{O_2}} p_{CO} \sqrt{p_{O_2}}}{1 + b_{CO} p_{CO}} \approx \text{const}$$



↳ CO-Ox. auf Pt LH-Mechanismus!

### Oxidische Oberflächen

z.B. Oxidative Dehydr. von Propan an Vanadiumoxiden

