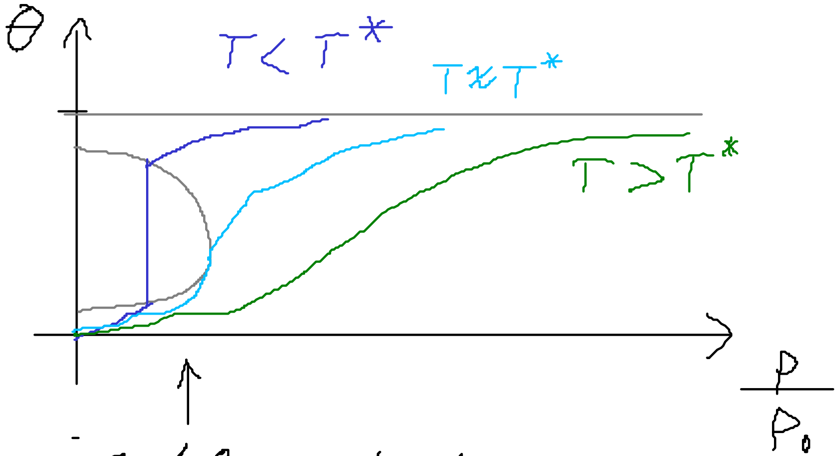
letzte mal: Fowler – Isotherme

$$p = \frac{\theta}{1-\theta}\, p_0(T)\, \exp\left(-\frac{z\,\gamma\,\theta\,\varepsilon}{kT}\right)$$




instabiler Zustand
= Kondensation

## Adsorptionswärme

Gibbs – Adsorptionsgleichung

$$S_s\, dT + \sum_i N_{is}\, d\mu_i + A\, d\gamma = 0$$

Dichte $\frac{S_s}{A} = s_s$ $\quad \frac{N_{is}}{A} = n_{is}$

$$d\gamma = -s_s\, dT - \sum_i n_{is}\, d\mu_i$$

$$d\gamma = -\sum_i n_i\, d\mu_i \qquad \text{freie Energie}$$

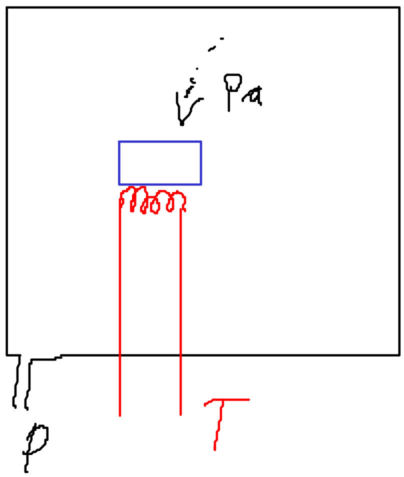
$$n_{is} = -\left.\frac{\partial \gamma}{\partial \mu}\right|_{T,\mu_j}\Big|_{j \neq i}$$ alle anderen chem. Potentiale bleiben konstant

$$\mu_i = \mu_0 - kT\ln(p_i)$$

chem. Potential bei best. Druck

chem. Pot. bei Partialdruck $p_i$

$$\partial\mu_i = kT\,\partial\ln(p_i) \Rightarrow n_{is} = -\frac{1}{kT}\left(\frac{\partial}{\partial\ln(p_i)}\right)_{T,p_j}$$




Oberfläche

$$\theta(t)\,,\quad \theta = \text{const} = \theta(p,T)$$

$$\Rightarrow \bar{Q}_{ads}$$ adsorptionswärme

$$\theta \Rightarrow n_{as}$$ ersetzen

$$d\mu_a = \left.\frac{\partial\mu_a}{\partial T}\right|_{n_{as}\,A} dT$$

$$dF = s_s\,dT + \sum_i \mu_i\,dN_{is} + \gamma\,dA$$

$$\mu_a = \left.\frac{\partial F}{\partial N_{as}}\right|_{T,A}$$

$$d\mu_a = \frac{\partial}{\partial T}\left[\left.\frac{\partial F}{\partial N_{as}}\right|_{T,A}\right]dT = \frac{\partial}{\partial N_{as}}\left[\left(\frac{\partial F}{\partial T}\right)_{N_{as},T}\right]dT$$

$$= -\bar{S}_{as}\,dT \qquad = d\mu_a$$

$$dE = \delta W + \delta Q = -p\,dV + \sum_i \mu_i\,dN_{is} + \gamma\,dA + T\,dS$$

Oberflächenenergie

$$E_{av} = -p_a V_a + \mu_a N_{av} + T S_{av}$$

$$N_{av}\,dN = dE_{av} + p_a\,dV_{av} + V_{av}\,dp_a - T\,dS_{av} - S_{av}\,dT$$

$$dE = T\,dS_{av} - p_a\,dV_a \Rightarrow d\mu_a = \frac{1}{N_{av}}\left(V_a\,dp_a - S_{av}\,dT\right)$$

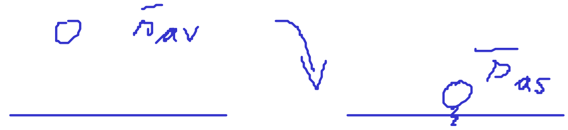
$$= \bar{v}_a\,dp_a - \bar{s}_{av}\,dT$$

$\bar{x} = \frac{x}{N}$, pro Teilchen

$$-\bar{s}_{as}\,dT = -\bar{s}_{av}\,dT + \bar{v}_a\,dp_a$$

$$\Rightarrow \left(\frac{dp}{dT}\right) = -\frac{\bar{s}_{as} - \bar{s}_{av}}{\bar{v}_a} = -\frac{\bar{q}_a}{T\,\bar{v}_a}$$

Änderung der Entropie vor zu auf der Oberfläche




$$\left(\frac{dp_a}{dT}\right)_{n_{as}} = -\frac{\bar{q}_{ads}}{T\,\bar{V}_a}$$

$$\boxed{\left.\frac{\partial \ln(p_a)}{\partial T}\right|_{n_{as}}} = \frac{1}{p_a}\left(\frac{\partial p_a}{\partial T}\right)_{n_{as}} = -\frac{\bar{q}_{ads}}{T\,\bar{v}_a} = -\frac{\bar{q}_{ads}}{k_B T^2}$$

$$\boxed{= -\frac{\bar{Q}_{ads}}{N_{av}\,k_B T^2}}$$ molare Adsorptionswärme

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

$$p = \frac{\theta}{1-\theta}\, p_0 \exp(-\beta\, z Z \varepsilon\, \Theta)$$

$$\ln p = \ln\frac{\theta}{1-\theta} + \ln(p_0(T)) - \frac{z Z \varepsilon \theta}{kT}$$

$$\frac{\ln p}{\partial T} = 0 + \frac{\partial \ln(p_0)}{\partial T} + \frac{z Z \varepsilon \theta}{k T^2}$$

$$\ln p_0 = \dots$$

$$\Rightarrow \frac{\partial \ln p_0}{\partial T} = \frac{3}{2}\frac{1}{T} + \frac{1}{T} + \frac{\varepsilon_a}{kT^2} = \frac{5}{2}\frac{1}{T} + \frac{\varepsilon_a}{kT^2}$$

$$\frac{\partial \ln p}{\partial T} = \frac{5}{2T} + \frac{\varepsilon_a}{kT^2} + \frac{2 z \varepsilon \Theta}{kT^2}$$

$$\Rightarrow \bar{Q}_{ads} = -N_a\, kT^2 \left( \frac{5}{2T} + \frac{\varepsilon_a}{kT^2} + \frac{2 z \varepsilon \Theta}{kT^2} \right)$$

$$\bar{Q}_{ads} = -N_a \left( \underbrace{\frac{5}{2} kT + \varepsilon_a}_{\text{Langmuir-Beitrag für } \varepsilon = 0} + 2 z \varepsilon \Theta \right)$$

$\varepsilon_p$ WW der Teilchen untereinander

Koordinationszahl $z$

thermale Desorption (Folie)

Messung $\Rightarrow$ Temperatur durchfahren, dabei Desorption messen $\Rightarrow$ Bindungsenergien

+ Modell für WW der Adsorbate untereinander