

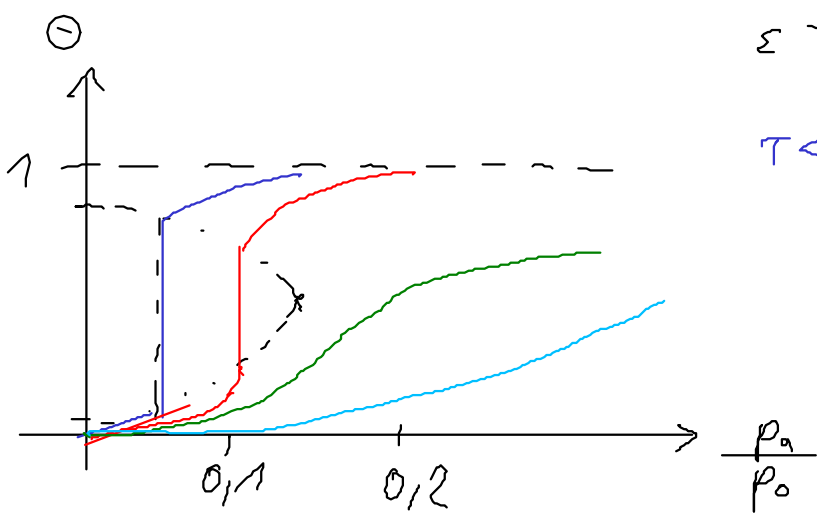
2D-Gas Modell



$$Z[\epsilon_a, \epsilon, Z] \Rightarrow p_a = \frac{\theta}{1-\theta} \exp\left[-\frac{eZ\theta\epsilon}{kT}\right]$$

2 dimensional
 $\theta_{max} = 1$
 $T^* = \frac{Z\epsilon}{2k}$

$\epsilon > 0$
 $T < T^*$



$$S_S dT + \sum_i N_{iS} d\mu_i + A d\delta = 0$$

$$d\delta = -S_S dT - \sum_i n_{iS} d\mu_i = -\sum_i n_{iS} d\mu_i$$

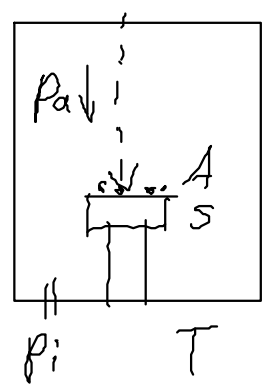
$$n_{iS} = -\left. \frac{\partial \delta}{\partial \mu_i} \right|_{T, \mu_j \neq i}$$

- Chemisches Potential $\mu_i = \mu_0 - kT \ln p_i$
- μ_0 Chemisches Potential bei einer Atmosphäre

$$d\mu_i = kT \ln p_i$$

$$\Rightarrow n_{iS} = -\frac{1}{kT} \left(\frac{\partial \delta}{\partial \ln p_i} \right)_{T, p_j \neq i}$$

Isostere



$\theta(T)$ konstant halten
 $\Rightarrow \theta_{const}(p, T) \rightarrow$ was
 Adsorptionswärme \bar{q}_{ads} eraren
 bestimmt werden

$$\partial \mu_a = \left(\frac{\partial \mu_a}{\partial T} \right)_{N_{as}, A} dT$$

$$dF_s = -\bar{S} dT + \sum \mu_i dN_{is} + \delta A$$

$$\mu_a = \left(\frac{\partial F_s}{\partial N_{as}} \right)_{T, A}$$

$$\partial \mu_a = \frac{\partial}{\partial T} \left(\left(\frac{\partial F_s}{\partial N_{as}} \right)_{T, A} \right) dT = \frac{\partial}{\partial N_{as}} \left(\left(\frac{\partial F_s}{\partial T} \right)_{N_{as}, T} \right) dT = -\bar{S}_{as} dT$$

$$\partial \mu_a = -\bar{S}_{as} dT \quad \text{auf der Oberfläche}$$

1. Hauptsatz Thermodynamik

$$dE = dW + dQ = p dV + \sum \mu_i dN_{is} + \delta A + T dS$$

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

Zone vor der Oberfläche

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

$$dE_{av} = T dS_{av} - p_a dV_a \quad \text{pro 1 Teilchen}$$

$$\Rightarrow \partial \mu_a = \frac{1}{N_{av}} (V_a dp_a - S_{av} dT) = \frac{1}{N_{av}} d p_a - \frac{1}{N_{av}} d S_{av}$$

$$-\bar{S}_{as} dT = -\bar{S}_{av} dT + \bar{V}_a dp_a$$

$$\boxed{\left(\frac{\partial p_a}{\partial T} \right)_{mas} = - \frac{\bar{S}_{as} - \bar{S}_{av}}{\bar{V}_a} = - \frac{\bar{q}_{ads}}{T \bar{V}_a} \quad \text{Gibbs}}$$

$$\left(\frac{\partial \ln p_a}{\partial T} \right)_{mas} = \frac{1}{p_a} \left(\frac{\partial p_a}{\partial T} \right)_{mas} = - \frac{\bar{q}_{ads}}{T \bar{V}_a} = - \frac{\bar{q}_{ads}}{k T^2} = - \frac{Q_{ads}}{N_a k T^2}$$

• Molare Adsorptionswärme \bar{q}_{ads}

• Avogadro Zahl N_a

Beispiel

$$\text{isotherme: } p_0(T) = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} k T \exp\left[-\frac{\epsilon_a}{k T}\right]$$

$$p = \frac{\theta}{1-\theta} p_0 \exp\left[-\frac{2Z\epsilon\theta}{k T}\right]$$

$$\ln p = \ln \frac{\theta}{1-\theta} + \ln p_0(T) - \frac{2Z\varepsilon\theta}{kT}$$

$$\frac{\partial \ln p}{\partial T} = 0 + \frac{\partial \ln p_0}{\partial T} + \frac{2Z\varepsilon\theta}{kT^2}$$

$$\ln p_0 = \dots$$

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

$$\frac{\partial \ln p}{\partial T} = \frac{5}{2} \frac{1}{T} + \frac{\varepsilon_a}{kT^2} + \frac{2Z\varepsilon\theta}{kT^2}$$

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

$$\bar{Q}_{ads} = -N_a \left(\underbrace{\frac{5}{2} kT + \varepsilon_a}_{\text{Langmuir}} + \underbrace{2Z\varepsilon\theta}_{\text{laterale WW}} \right)$$

- $\varepsilon = 0$: keine Wechselwirkung \Rightarrow Langmuir
- $\varepsilon > 0$: attraktive WW

Höflich ist Paare zu bilden $Z \} \sim \bar{Q}_{ads}$
 Bede ε und θ

Thermodynamik der Adsorption

Thermal Desorption

- $\nu(\theta)$ Frequenz der Schwingung bei bestimmter Bedeckung θ des Adsorbats

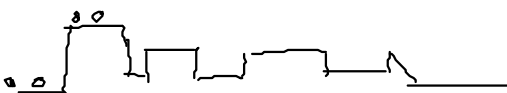
$$\frac{d\theta}{dt} = -\nu(\theta) \theta^u \exp \left[-\frac{\varepsilon_a(\theta)}{RT} \right]$$

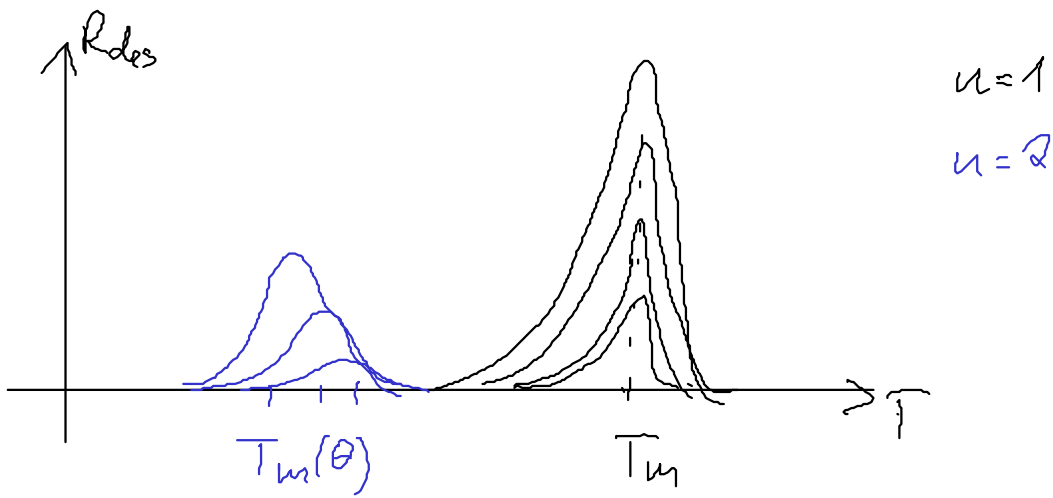
- exp. Aufbau

Thermoelement zur Messung der Temperatur $T = T_a + \beta t$

Quadrupol-Klass-Spektrometer: $R_{des}(T)$

- Bindungsenergie ist Breite Verteilung $\Rightarrow R_{des}(T)$ breite Peaks





- Aktivierung E für die Desorption i. A. $E \neq E_a$
 - \Rightarrow Verknüpfung von Adsorptionsenergie mit Position von T_m .
 - \Rightarrow Bindungsenergie pro Teilchen (lokalisierte Adsorption) kleiner Moleküle
- Desorption abhängig von Position an Oberfläche