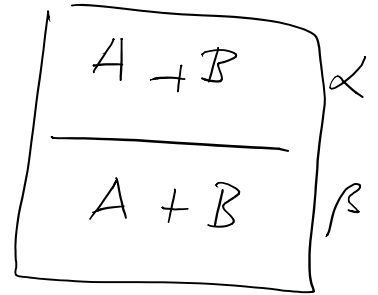


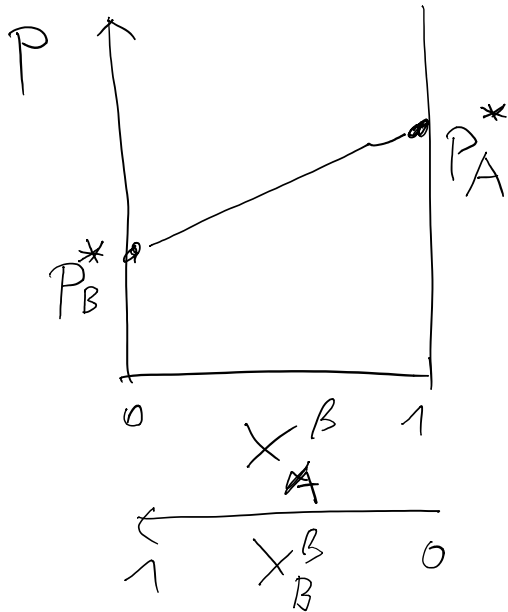
Dampfdruck von Mischungen

Montag, 8. Juni 2015 13:12

$$\mu_{\text{Misch}}^{A\alpha} = \underbrace{\mu_{\text{rein}}^{A\alpha}}_{G_A^m} + \underbrace{RT \ln a_A^{\alpha}}_{< 0}$$



ideale Mischungen: $a_A \rightarrow X_A^{\alpha}$



bei fester T

$$P(X_A^{\alpha})(X_B^{\alpha})?$$

$$X_A^{\alpha} = \frac{P_A^* X_A^{\beta}}{P_B^* + (P_A^* - P_B^*) X_A^{\beta}}$$

$\underbrace{\hspace{10em}}_{\text{gas}}$
 $\underbrace{\hspace{10em}}_{\text{flüssig}}$

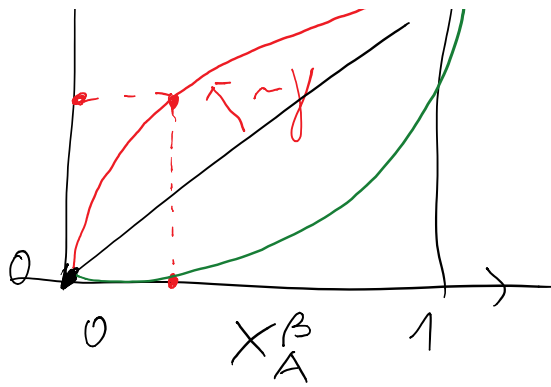
$$P_A^* > P_B^* \\ P_A^* < P_B^* \\ X_A^{\alpha} =$$

$$y = \frac{P_A^*}{P_B^*} > 1$$

$$X_A^{\alpha} = \frac{\frac{P_A^*}{P_B^*} \cdot X_A^{\beta}}{1 + \left(\frac{P_A^*}{P_B^*} - 1\right) X_A^{\beta}}$$



$$X_A^{\alpha} = \frac{y X_A^{\beta}}{1 + (y-1) X_A^{\beta}} > X_A^{\beta}$$



$$X_A^\alpha = \frac{0 \cdot 1}{1 + \underbrace{(\gamma - 1)}_{> 0} X_A^\beta} \geq X_A^\beta$$

$$X_A^\alpha = X_A^\beta \text{ falls}$$

$$\gamma \rightarrow X_A^\beta = 0$$

$$X_A^\beta = 1$$

$$X_A^\alpha = \frac{\gamma \cdot 1}{1 + \gamma - 1}$$

$$= 1$$

Auflösen nach X_A^β :

$$X_A^\alpha (P_B^* + (P_A^* - P_B^*) X_A^\beta) = P_A^* X_A^\beta$$

$$P_B^* X_A^\alpha = P_A^* X_A^\beta - (P_A^* - P_B^*) X_A^\alpha X_A^\beta$$

$$P_B^* X_A^\alpha = X_A^\beta (P_A^* + (P_B^* - P_A^*) X_A^\alpha)$$

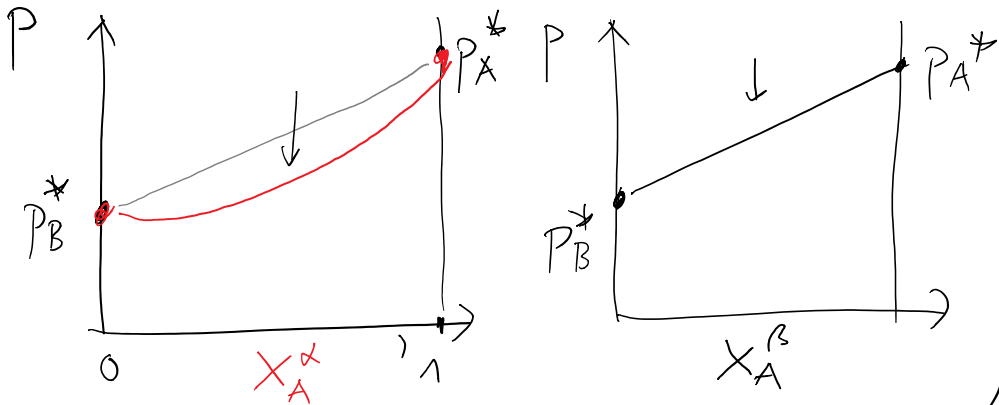
$$X_A^\beta = \frac{P_B^* X_A^\alpha}{P_A^* + (P_B^* - P_A^*) X_A^\alpha} \quad *$$

$$X_A^\beta = \frac{X_A^\alpha}{P_A^*} \cdot P \quad \text{Raoult'sches Gesetz}$$

$$\frac{X_A^\beta}{P_A^*} \cdot P = \frac{P_B^* X_A^\alpha}{P_A^* + (P_B^* - P_A^*) X_A^\alpha}$$

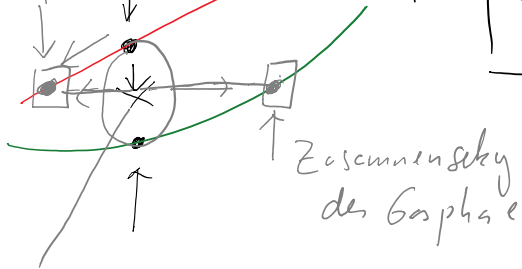
$$\rightarrow P = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) X_A^\alpha}$$

 bekannte Größen

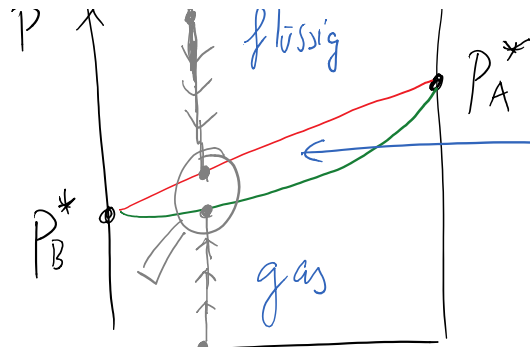


$X_A^\alpha = X_A^\beta = 0.3$
 \downarrow flüssig \uparrow P_A^*

Zusammensetzung von Flüssigkeit



2 Phasen - Bereich



Mischung aus Flüssig und Gas

$X_A^\alpha \rightarrow$
 $X_A^\beta \rightarrow$

Beispiel CO₂ in Atmosphäre
(H₂O)

$$X_{CO_2}^g = \frac{P_{CO_2}}{P}$$

$$P_{CO_2} = 3 \cdot 10^{-4} \text{ bar}$$

$$P = 1 \text{ bar}$$

$$\hookrightarrow X_{CO_2}^g = 3 \cdot 10^{-4}$$

$$X_{CO_2}^l = \frac{P_{CO_2}}{P_{CO_2}^*}$$

$$P_{CO_2}^* = 40 \text{ bar}$$

(bei 5°C)

$$X_{CO_2}^l = 7.5 \cdot 10^{-6}$$

Mengenverhältnis $m_{CO_2}^g$, $m_{CO_2}^l$

$$\frac{m_{CO_2}^g}{M_{CO_2}} = n_{CO_2}^g = \frac{P_{CO_2} \cdot V_{Atm}}{R \cdot T} \quad T = 288K$$

ideales Gasgesetz

$$V_{Atm} = 4\pi R_{erde}^2 \cdot 8km$$

$$m_{CO_2}^g = 2.3 \cdot 10^{15} \text{ kg}$$

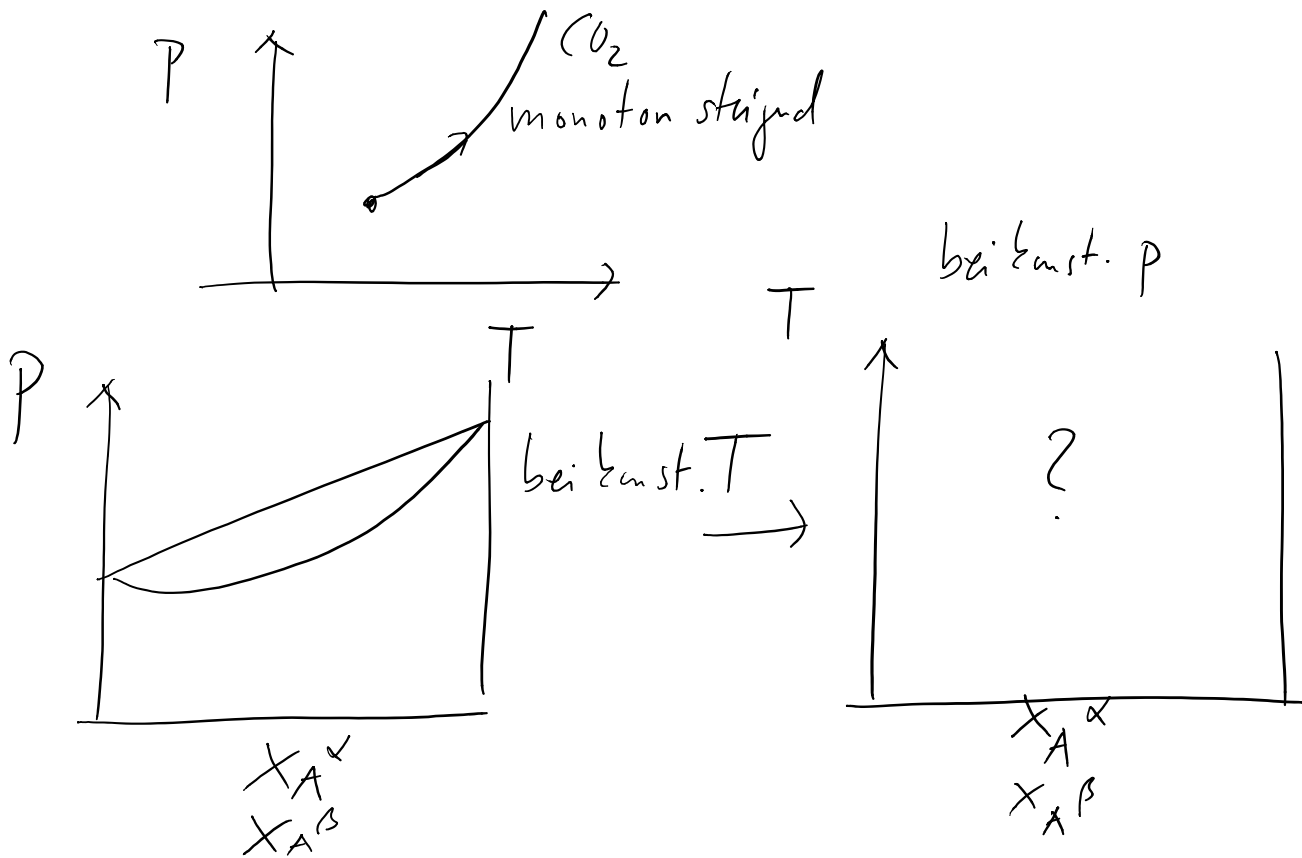
$$n_{gas} \approx n_{H_2O}$$

$$\frac{m_{CO_2}^g}{M_{CO_2}} = n_{CO_2}^g = X_{CO_2}^g \cdot n_{H_2O}^g$$

$$V_{meer} = 14 \cdot 10^8 \text{ m}^3$$

$$m_{CO_2}^g = 2.5 \cdot 10^{16} \text{ kg}$$

$$X_{CO_2}^g = \frac{P_{CO_2}}{P}$$



Beschreibung von $T(x_A^\alpha) / T(x_A^\beta)$

($p = \text{konst}$)

$$d\left(\frac{M_A^\alpha}{T}\right) = d\left(\frac{M_A^\beta}{T}\right) \quad T^\alpha = T^\beta$$

$$d\left(\frac{M_A^{\alpha*}}{T}\right) + R \cdot d \ln(x_A^\alpha) = d\left(\frac{M_A^{\beta*}}{T}\right) + R d \ln(x_A^\beta)$$

Gibbs-Helmholtz Gleichung $\frac{d}{dT} \left(\frac{M_A^{\alpha*}}{T} \right) = - \frac{H_A^{\alpha*}}{T^2}$

$$- \frac{H_A^{\alpha*}}{T^2} dT + R d \ln(x_A^\alpha) = - \frac{H_A^{\beta*}}{T^2} dT + R d \ln(x_A^\beta)$$

$$R d \ln\left(\frac{x_A^\alpha}{x_A^\beta}\right) = \frac{H_A^{\alpha*} - H_A^{\beta*}}{T^2} dT$$

$$\underset{l}{\beta} \rightarrow \underset{g}{\alpha} \quad H_A^{\alpha*} - H_A^{\beta*} = \Delta_V H_A$$

$$d \ln\left(\frac{x_A^\alpha}{x_A^\beta}\right) = \frac{\Delta_V H_A}{R} \frac{1}{T^2} dT$$

$$\Delta_V H_A \neq f(T)$$

$$\int_1^{x_A^\alpha/x_A^\beta} d \ln\left(\frac{x_A^\alpha}{x_A^\beta}\right) = \frac{\Delta_V H_A}{R} \int_{T_A^*}^T \frac{1}{T'^2} dT'$$

$$\ln\left(\frac{x_A^\alpha}{x_A^\beta}\right) = \frac{\Delta_V H_A}{R} \left\{ -\frac{1}{T} + \frac{1}{T_A^*} \right\}$$

$$\boxed{\ln\left(\frac{x_A^\alpha}{x_A^\beta}\right) = \frac{\Delta_V H_A}{R} \frac{T - T_A^*}{T \cdot T_A^*}}$$

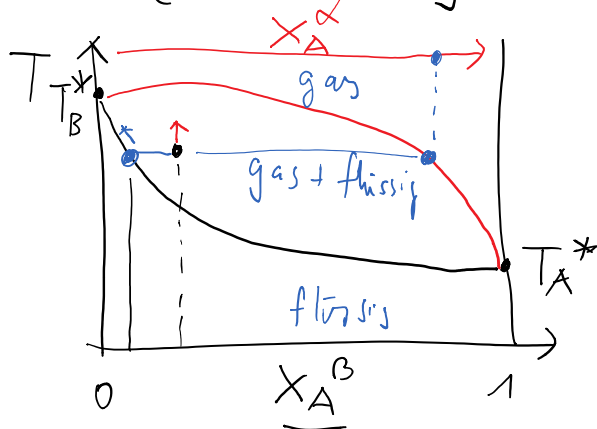
$$\ln\left(\frac{X_A^\alpha}{X_A^\beta}\right) = \frac{\Delta_v H_A}{R} \frac{T - T_A^*}{T \cdot T_A^*}$$

$$\ln\left(\frac{X_B^\alpha}{X_B^\beta}\right) = \frac{\Delta_v H_B}{R} \frac{T - T_B^*}{T \cdot T_B^*}$$

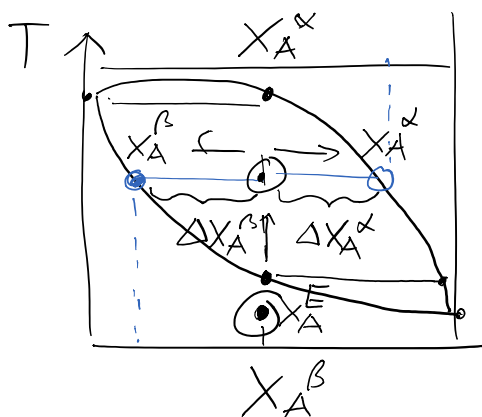
$$X_A^\alpha = 1 - X_B^\alpha$$

$$X_A^\beta = 1 - X_B^\beta$$

$$T \in \{T_A^* \dots T_B^*\}$$



Wie bekommen wir die Mole von n_A^β und n_A^α ?



X_A^E : Wert des Molenbruchs wenn nur Gasphase
oder nur Flüssig

$$n_A = n_A^\alpha + n_A^\beta$$

$$n_A \cdot X_A^E = n_A^\alpha \cdot X_A^E + n_A^\beta \cdot X_A^E$$

$$- n_A \cdot X_A^E = n_A^\alpha \cdot X_A^\alpha + n_A^\beta \cdot X_A^\beta$$

$$0 = n_A^\alpha (X_A^E - X_A^\alpha) + n_A^\beta (X_A^E - X_A^\beta)$$

$$n_A^\alpha (X_A^E - X_A^\alpha) = n_A^\beta (X_A^\beta - X_A^E)$$

$$n_A^\alpha (X_A^E - X_A^\alpha) = n_A (X_A - X_A^\alpha)$$

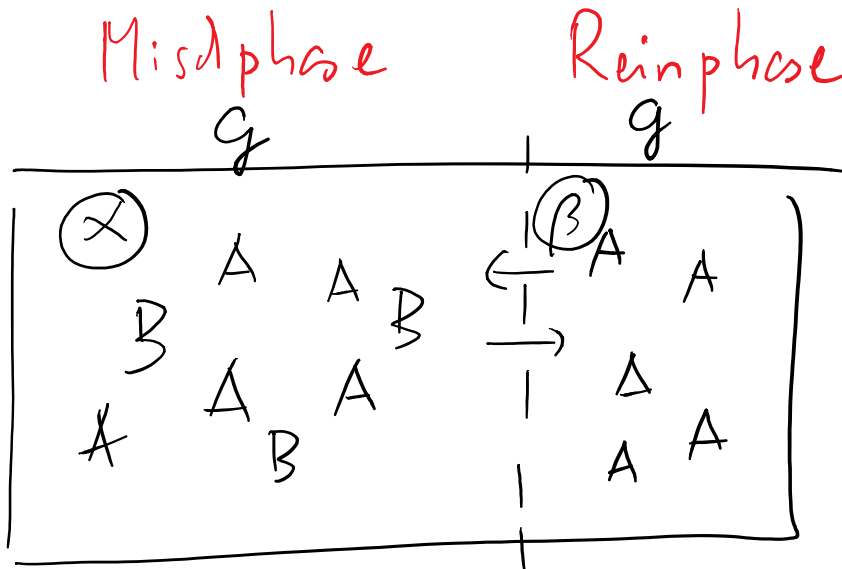
$\underbrace{\hspace{10em}}_{\Delta X_A^\alpha} \qquad \qquad \qquad \underbrace{\hspace{10em}}_{\Delta X_A^\beta}$

$$\frac{n_A^\alpha}{n_A^\beta} = \frac{\Delta X_A^\beta}{\Delta X_A^\alpha}$$

Wenn Gesamtstoffmenge
bekannt n_A und X_A^E
kann n_A^α und n_A^β bestimmt
werden

Gasphasen-Mischung

Mittwoch, 10. Juni 2015 12:50



TD-Gleichgewicht Semipermeable Wand

$$T_\alpha = T_\beta = T$$

$$\mu_A^\alpha = \mu_A^\beta$$

$$\rightarrow p_A^\alpha = p_A^\beta = p_A$$

$$p^\alpha = \sum_i p_i^\alpha \quad (2 \text{ Komponenten A und B})$$

$$= p_A^\alpha + p_B^\alpha$$

> 0

$$p^\beta = p_A^\beta = p_A$$

$$p^\alpha > p^\beta$$

$$\mu_A^\alpha = \mu_A^\beta$$

$$\mu_A^\alpha(p, T) = \mu_A^{\beta^*}(p_A, T) \quad (1)$$

bei konst. T gilt

$$d\mu = \left(\frac{\partial \mu}{\partial p} \right)_T dp$$

$$V^m = \frac{R \cdot T}{p} \quad (\text{ideales Gas})$$

$$\int_I^{\text{II}} d\mu = RT \int_I^{\text{II}} \frac{1}{p} dp$$

$$\mu(\text{II}) - \mu(\text{I}) = RT \ln \left(\frac{p_{\text{II}}}{p_{\text{I}}} \right)$$

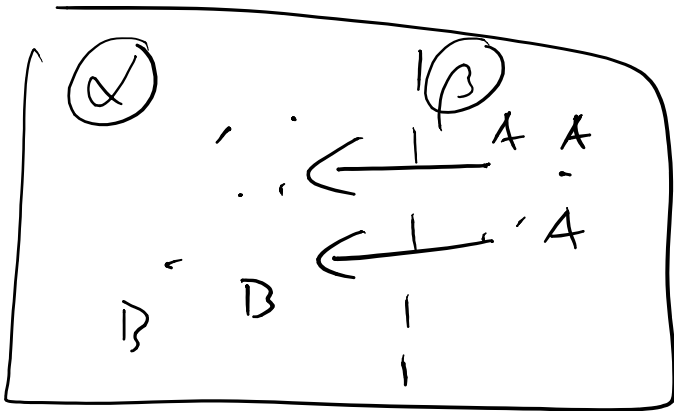
$$\text{also: } \mu_A^{\beta^*}(p_A, T) = \mu_A^{\beta^*}(p, T) + RT \ln \left(\frac{p_A}{p} \right)$$

$$M_A^\alpha(p, T) = M_A^{\beta^*}(p, T) + RT \ln\left(\frac{p_A}{p}\right)$$

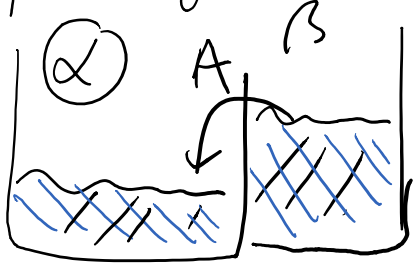
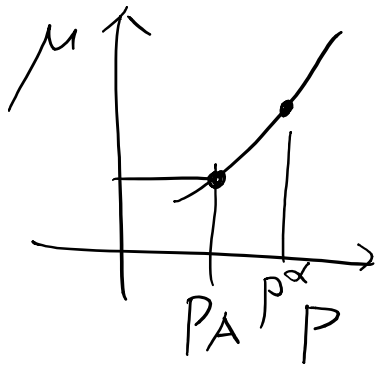
Mischphase

Reine Phase

X_A^α
 < 0

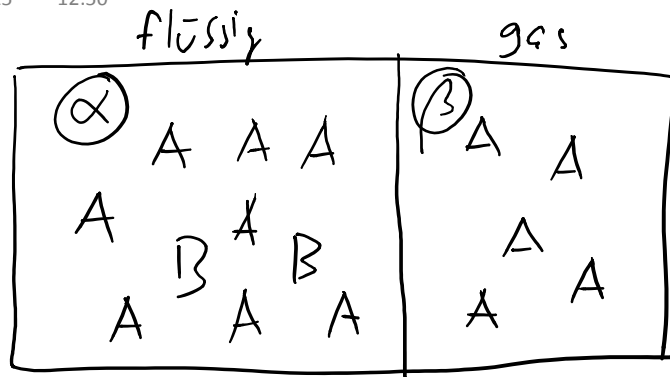


$M_A^\alpha < M_A^\beta$
 p^α steigen p^β fallen



Dampfdruckerniedrigung

Mittwoch, 10. Juni 2015 12:50



$$d\mu_A^\alpha = d\mu_A^{\beta*}$$

$$a_A = f_A \cdot X_A$$

für ideale Mischung

$$f_A = 1$$

$$a_A = X_A$$

$$d\mu_A^{\alpha*} + RT d \ln a_A = d\mu_A^{\beta*}$$

$$\underbrace{\left(\frac{\partial \mu_A^{\alpha*}}{\partial p} \right)_T}_{V_A^{m\alpha*}} dp = \underbrace{\left(\frac{\partial \mu_A^{\beta*}}{\partial p} \right)_T}_{V_A^{m\beta*}} dp$$

$$RT d \ln a_A = \underbrace{(V_A^{m\beta*} - V_A^{m\alpha*})}_{\text{ideales Gasgesetz}} dp$$

$$V_A^{m\beta*} = \frac{RT}{p} \quad \text{ideales Gasgesetz}$$

$$V_A^{m\alpha*} \ll V_A^{m\beta*}$$

$$\cancel{RT} \cdot d \ln a_A = \frac{\cancel{RT}}{p} dp$$

a_A p_A

$$\text{Reinstoff} \rightarrow \int_1^{q_A} d \ln q_A = \int_{P_A^*}^{P_A} \frac{1}{P} dp$$

$$e^{\ln q_A} = e^{\ln \left(\frac{P_A}{P_A^*} \right)}$$

$$q_A = \underbrace{f_A}_{\text{Bestimmbar}} \cdot \underbrace{X_A}_{\text{bekannt}} = \frac{\underbrace{P_A}_{\text{bekannt}}}{\underbrace{P_A^*}_{\text{bekannt}}}$$

$$\frac{P_A}{P_A^*} = 1 - X_B^B$$

Dampf-
Druck-
Erhöhung

$$X_B = 1 - \frac{P_A}{P_A^*} = \frac{P_A^* - P_A - \Delta P}{P_A^*} = \frac{\Delta P}{P_A^*}$$

$$X_B \sim \frac{\Delta P}{P_A^*}$$

$$\Delta P \sim P_A^* \cdot X_B$$

$$\Delta p \sim p_A \cdot X_B$$

Dampfdruck erniedrigung hängt nicht von der Art des Stoffes B ab, sondern nur vom Molenbruch X_B

(Kolligative Eigenschaft)

