Gibbs Duhem

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T, P keine Fktn. von n

$\rightarrow V, U, H, G, \mu$ sind Fktn von n

$$V = n_1 V_1^m + n_2 V_2^m = \sum_i n_i V_i^m$$

$$dV = dn_1 V_1^m + dn_2 V_2^m + n_1 dV_1^m + n_2 dV_2^m$$

$$dV = \underbrace{\left(\frac{\partial V}{\partial n_1}\right)_{n_2}}_{V_1^m} dn_1 + \underbrace{\left(\frac{\partial V}{\partial n_2}\right)_{n_1}}_{V_2^m} dn_2$$

$$\Rightarrow \boxed{n_1 dV_1^m + n_2 dV_2^m = 0}$$

verallgemeinert $\sum_i n_i dV_i^m = 0$

$$\boxed{\sum_i n_i d\mu_i = 0}$$ Gibbs-Duheme Gl.

Mischung von Gasen

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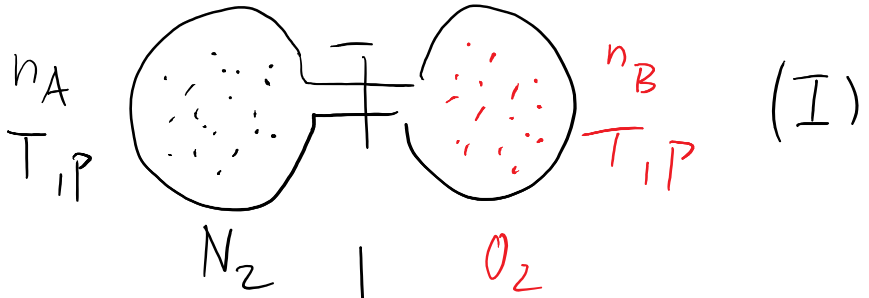

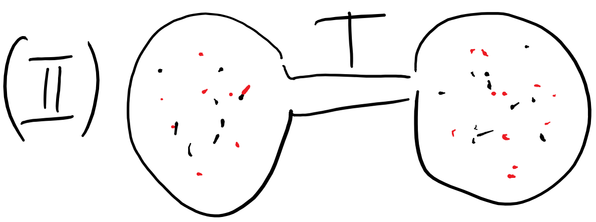

T

$p = p_A + p_B$

p_A : Partialdruck von Stoff A

p_B : "

Molenbruch $x_i = \frac{p_i}{p}$

$$x_A = \frac{p_A}{p} = \frac{p_A}{p_A + p_B}$$

$$\boxed{G_m(p) = G_m^0 + RT\ln\left(\frac{p}{p_0}\right)}$$

p_0 : Standard-Druck $\qquad \frac{\partial G}{\partial p} = \left(V_m = \frac{nRT}{p}\right)$

G_m^0 : Standard-Gibbs Energie

$$\mu_A(p) = \mu_A^0 + RT\ln\left(\frac{p}{p_0}\right)$$

$$\mu_B(p) = \mu_B^0 + RT\ln\left(\frac{p}{p_0}\right)$$

Gibbs-Energie für Zustand (I) {vor Mischung}

$$G_I = n_A\mu_A + n_B\mu_B$$

$$= n_A\left(\mu_A^0 + RT\ln\left(\frac{p}{p_0}\right)\right)$$

$$+ n_B\left(\mu_B^0 + RT\ln\left(\frac{p}{p_0}\right)\right)$$

{nach Mischen}

$$G_{II}$$

$$= n_A\left(\mu_A^0 + RT\ln\left(\frac{p_A}{p_0}\right)\right) +$$

$$n_B\left(\mu_B^0 + RT\ln\left(\frac{p_B}{p_0}\right)\right)$$

$$\Delta_M G = G_{II} - G_I =$$

$$= n_A RT\ln\left(\frac{p_A}{p}\right) + n_B \cdot R \cdot T\ln\left(\frac{p_B}{p}\right)$$

$$(n = n_A + n_B) \quad \frac{p_A}{p} = x_A, \quad \frac{p_B}{p} = x_B \Rightarrow \frac{n_{AB}}{n}$$

$$= nRT\left\{\underbrace{x_A \cdot \ln x_A}_{<0} + \underbrace{x_B\ln x_B}_{<0}\right\}$$

$$x_i \in \{0 \ldots 1\}$$

$$\boxed{\Delta_M G < 0}$$

$$\boxed{\Delta_M}$$

$$\Delta_M S = -\left(\frac{\partial \Delta_M G}{\partial T}\right)_{p, n_A, n_B}$$

$$\Delta_M S = -nR\left\{\underbrace{x_A \ln x_A}_{<0} + x_B \ln x_B\right\}$$

$$\boxed{\Delta_M S > 0}$$

$$\Delta_M G = \underbrace{\Delta_M H}_{=0} - T\Delta_M S$$

Mischung von Flüssigkeiten

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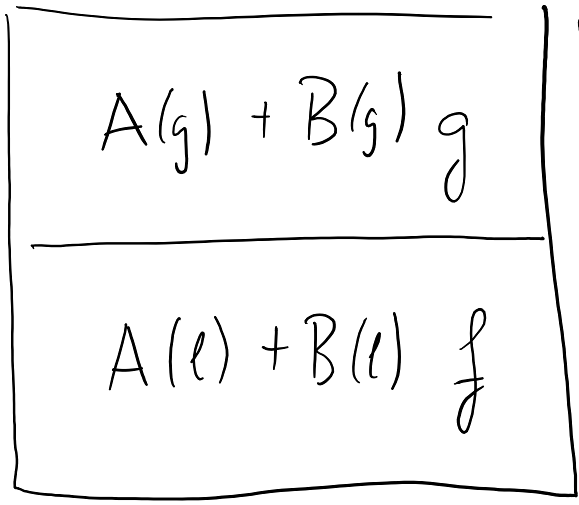
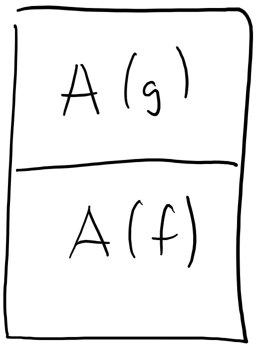


α-Phase

$\mu_A^\alpha, \mu_B^\alpha$

β-Phase

μ_A^β, μ_B^β



Reinstoff *

$$\mu_A^{\alpha *} = \mu_A^0 + RT \ln\left(\frac{p_A^*}{p_0}\right)$$

$$\mu_A^{\beta *} \overset{!}{=} \mu_A^{\alpha *} = \mu_A^0 + \underbrace{RT \cdot \ln\left(\frac{p_A^*}{p_0}\right)}$$

$$\hookrightarrow \mu_A^0 = \mu_A^{\beta *} - RT \ln\left(\frac{p_A^*}{p_0}\right)$$

<u>Mischung</u> :

Gasphase: $\mu_A^\alpha = \mu_A^{\alpha *} = \mu_A^0 + RT \ln\left(\frac{p_A}{p_0}\right)$

Flüssig: $\underbrace{\mu_A^\beta} = \mu_A^\alpha = \mu_A^0 + RT \ln\left(\frac{p_A}{p_0}\right)$

$$\mu_A^\beta = \mu_A^{\beta *} - RT \ln\left(\frac{p_A^*}{\cancel{p_0}}\right) + RT \ln\left(\frac{p_A}{\cancel{p_0}}\right)$$

$$\mu_A^\beta = \mu_A^{\beta *} + RT \ln\left(\frac{p_A}{\ldots}\right)$$

$$\boxed{\mu_A^\beta = \mu_A^{\beta *} + RT \ln\left(\frac{p_A}{p_A^*}\right)}$$

p_A : Dampfdruck von A in der Mischung

p_A^* : Dampfdruck von A in Reinphase

$$p_A \hookrightarrow p_A^*$$

Raoul Gesetz

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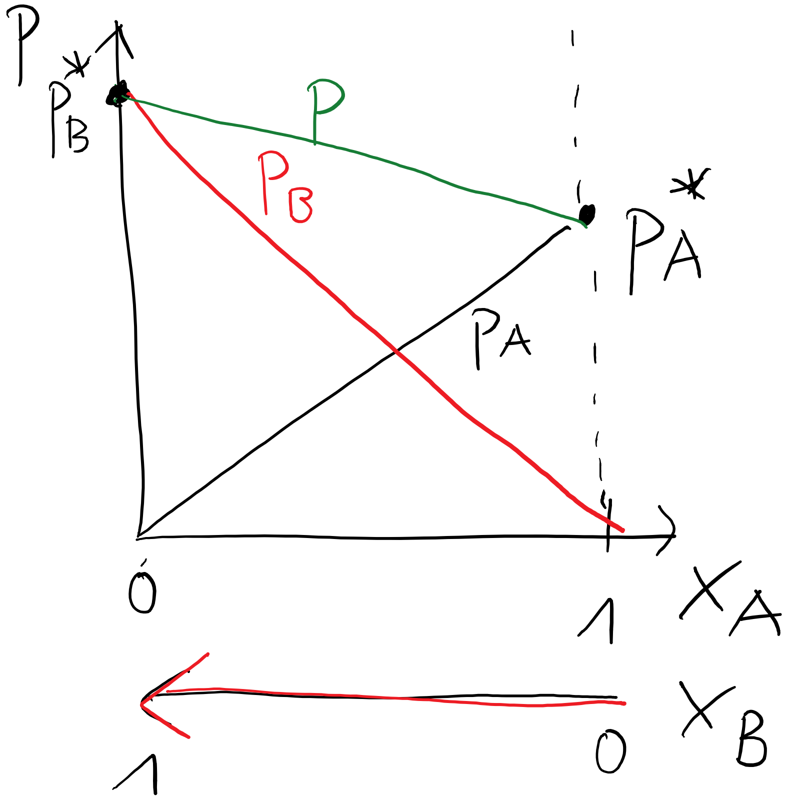
für ideale Mischungen gilt:

$$\boxed{p_A = p_A^* \cdot x_A}$$



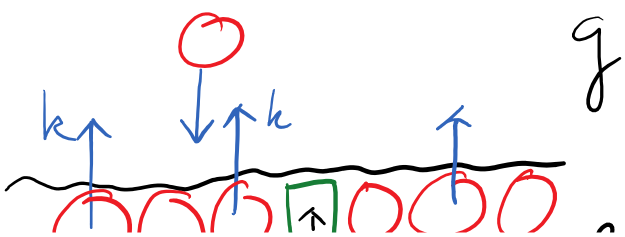
$$p = p_A + p_B$$

$$x_B = (1 - x_A)$$

ideale Mischung $\equiv$ WW zwischen

im Mittelwert $\overline{A-A} = \overline{A-B} = \overline{B-B}$

Molekulare Interpretation des Raoult-Gesetzes



Verdampfungsgeschwindigkeit $v_s = k\, x_A$

Kondensationsgeschwindigkeit $v_k = k' \cdot p_A$

TD-Gleichgewicht $v_s = v_k$

$$k \cdot x_A = k' \cdot p_A$$

$$p_A = \underbrace{\frac{k}{k'}} \cdot x_A$$

reine Flüssigkeit $x_A = 1 \rightarrow p_A^* = \frac{k}{k'}$

$$\boxed{p_A = p_A^* \cdot x_A}$$

Henry Gesetz

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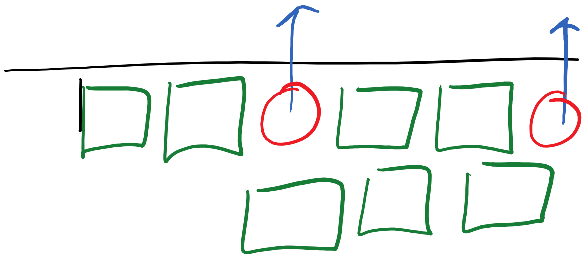


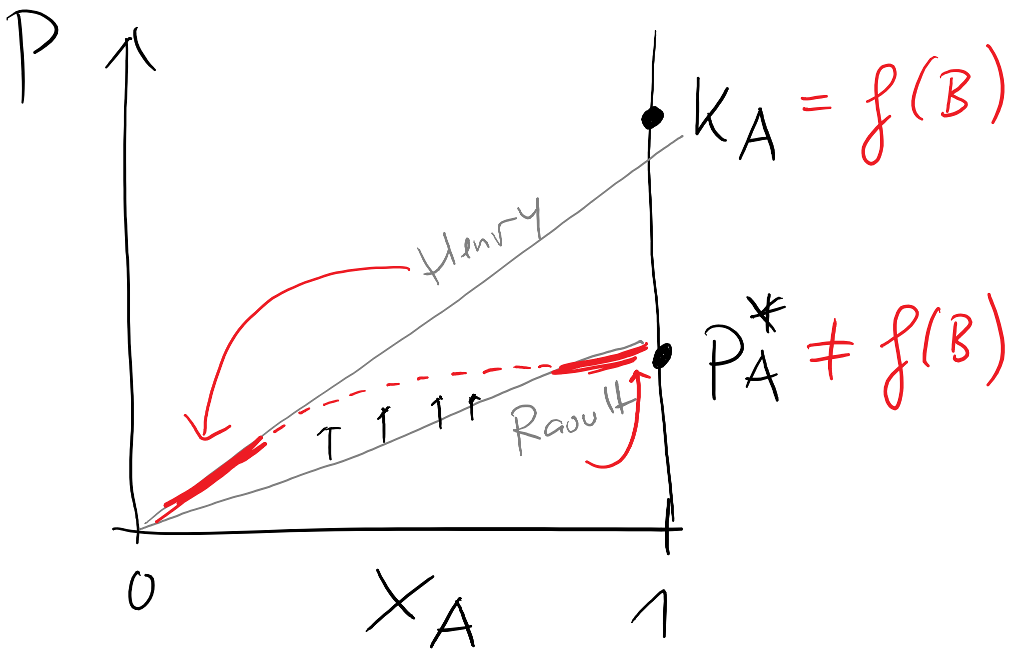
$$V_S = \underbrace{K''}_{\text{andere Prop. Konstante hängt von B ab}} \cdot x_A$$

$$\underbrace{V_K = K' \cdot p_A}$$

$$p_A = \underbrace{\frac{K''}{K'}}_{K_A} \cdot x_A$$

K_A Henry Konstante

$K_A \neq p_A^*$ außer $\overline{A-A} = \overline{A-B}$



Reale Mischungen

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$$\boxed{\mu_A = \mu_A^* + RT \ln a_A}$$

a_A = Aktivität des Stoffes A

$a_A = f_A \cdot x_A$ $\quad f_A$ Aktivitäts-Koeffizient

für ideale Flüssigkeiten gilt:

$$\Delta_M G = nRT\{x_A \ln x_A + x_B \cdot \ln x_B\}$$

$\Delta_M S$ wie Gasphase (ideal)

$\Delta_M H = 0 \quad , \quad \Delta_M V = 0 = \left(\frac{\partial \Delta_M G}{\partial p}\right)_T$

für reguläre Flüssigkeiten (WW $\overline{A-A} \neq \overline{A-B} = \overline{B-B}$, aber trotzdem noch statistische Verteilung der Moleküle A und B im Volumen gilt das nicht mehr:

$\Delta_M S$ (reg. Flüssigk.) $= \Delta_M S$ (ideal. Flüssig.)

$\Delta_M H$ (") $\neq 0$ im Allgemeinen

$\Delta_M V$ (") $\neq 0$

$$\Delta_{exzess} H = nRT \cdot \underset{\substack{\uparrow \\ \text{emp. Parameter}}}{\beta}\, x_A x_B$$

$$\Delta_M G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta \cdot x_A x_B\}$$

$\beta < 0$ exotherme Mischung $\quad \overline{A-B} > \overline{A-A}, \overline{B-B}$

$\beta < 0$ exotherm $\qquad$ B-B

$\beta > 0$ endotherm $\qquad <$

Beispiel: $\quad$ 1 mol H_2O in H_2O $\quad V_m = 18\,cm^3$ $\qquad \Delta_M V \neq 0$

1 mol H_2O in Ethanol $\quad V_m = 14\,cm^3$

PhasenGrenzen

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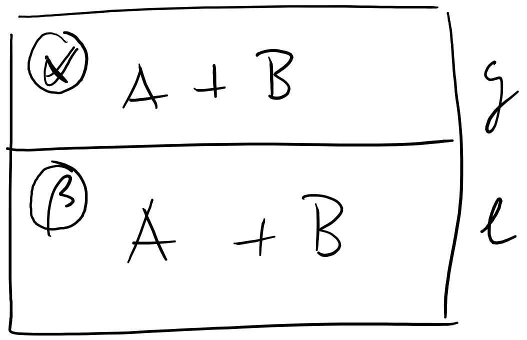


Gibbs Phasenregel

$$F = \underbrace{K}_{2} - \underbrace{P}_{2} + 2$$

$$F = 2$$

Zwei Parameter sind frei wählbar, alle anderen Größen sind dadurch festgelegt!

$$(p, T) \longrightarrow x_A^\alpha, x_A^\beta, x_B^\alpha, x_B^\beta, V$$

oder (p, x_A^α)

oder (p, x_A^β)

⋮

Bei konstanter Temperatur $(T = \text{konst})$ nur noch 1 freier Parameter, z.Bsp x_A^β

$$p(x_A^\beta) = \,?$$

$$p = p_A + p_B$$

ideale Mischung, d.h. $\begin{cases} p_A = p_A^* x_A^\beta \\ p_B = p_B^* x_B^\beta \end{cases}$

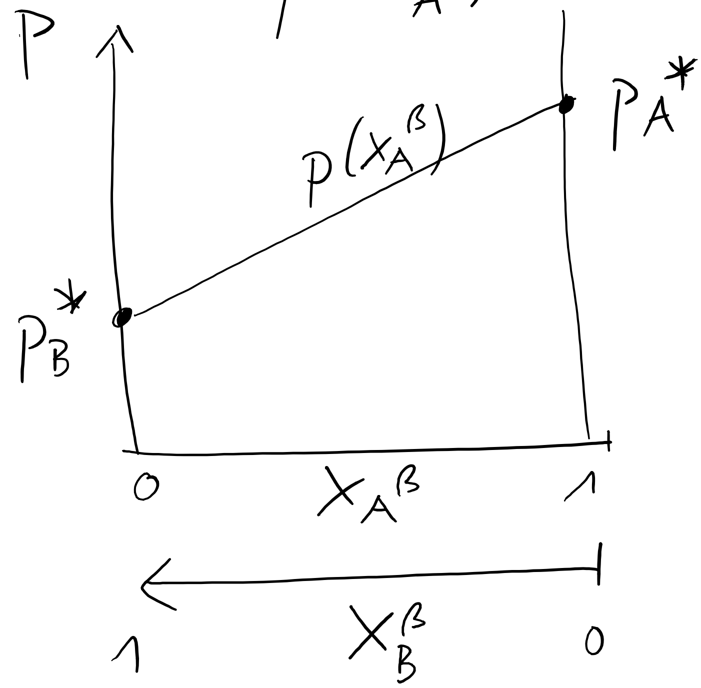
$$p = p_A \cdot x_A + p_B \quad B$$

$$\left(x_B^\beta = 1 - x_A^\beta \right)$$

$$p = p_A^* \cdot x_A^\beta + p_B^* \left(1 - x_A^\beta\right)$$

$$\boxed{p = p_B^* + \left(p_A^* - p_B^*\right) \cdot x_A^\beta}$$

$p(x_A^\beta)$



bei fester Temperatur T

$p(x_A^\alpha)$? $\qquad x_A^\alpha \neq x_A^\beta$ i. A.

<u>in der Gasphase gilt</u> (ideale Gase):

$$n^\alpha \frac{RT}{V} = p = p_A + p_B = n_A^\alpha \frac{RT}{V} + n_B^\alpha \frac{RT}{V}$$

$$n^\alpha = n_A^\alpha + n_B^\alpha \qquad \frac{n_A^\alpha}{n^\alpha} = x_A^\alpha = \frac{p_A}{p}$$

$$n^\alpha = n_A^\alpha + n_B^\alpha \qquad \frac{n_A^\alpha}{n} = X_A^\alpha = \frac{p_A}{p}$$

$$\frac{n_B^\alpha}{n} = X_B^\alpha = \frac{p_B}{p}$$

in der Flüssigkeit gilt: (ideale Flüssigkeiten)

$$p_A = p_A^* x_A^\beta$$

$$p_B = p_B^* \cdot x_B^\beta$$

$$x_A^\alpha = \frac{p_A}{p} = \frac{p_A}{p_A + p_B} =$$

$$= \frac{p_A^* x_A^\beta}{p_A^* \cdot x_A^\beta + p_B^* \cdot x_B^\beta}$$

$$x_B^\beta = (1 - x_A^\beta)$$

$$\rightarrow \boxed{x_A^\alpha = \frac{p_A^* x_A^\beta}{p_B^* + (p_A^* - p_B^*) x_A^\beta}}$$

Zusammenhang zw. x_A^α und x_A^β