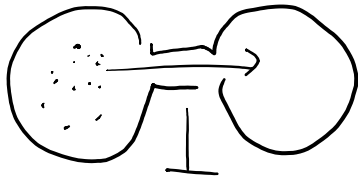


dU/dV



ideales Gas $T = \text{konst}$
 $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$dU = T dS - p dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p$$

Maxwell-Beziehung $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

Reales Gas: $\left(p + \frac{a}{V^2}\right)(V-b) = RT$

$$p = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{(V-b)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V-b} - p = \frac{\cancel{TR}}{V-b} - \frac{\cancel{RT}}{(V-b)} + \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

ideales Gas $a = 0$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$\backslash \partial v$

für $\text{reals } G_s \neq 0$

$$\left(\frac{\partial \mathcal{U}}{\partial v} \right)_T = 0$$

dS/dT

$$\left(\frac{\partial S}{\partial T}\right)_V \leftrightarrow C_V$$

$$dU = T dS - P dV$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$
$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dS = \frac{1}{T} \left[C_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T dV \right] + \frac{P}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T} \left(P + \left(\frac{\partial U}{\partial V}\right)_T \right) dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}} \quad \begin{array}{l} C_V > 0 \\ T > 0 \end{array} \quad \Delta S > 0$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\alpha} = - V \cdot \gamma \quad \text{aus Maxwell-Gleichung}$$

dH/dp

$$dH = T ds + V dp$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V$$

$$- \left(\frac{\partial V}{\partial T}\right)_p \quad \text{Maxwell Beziehung}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V$$

$\gamma \cdot V$

$$\left(\frac{\partial H}{\partial p}\right)_T = (-T\gamma + 1) \cdot V$$

Benzol (l) $\gamma = 1.23 \cdot 10^{-3} \frac{1}{K}$

25°C

$$\rho = 0.879 \frac{g}{cm^3}$$

$$M_{mol} = 78,11 g$$

$$V_m = \frac{M_{mol}}{\rho}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{M_{mol}}{\rho} (1 - T\gamma)$$

$$p_1 = 1 \text{ bar} \rightarrow p_2 = 11 \text{ bar}$$
$$\Delta p = 10 \text{ bar}$$

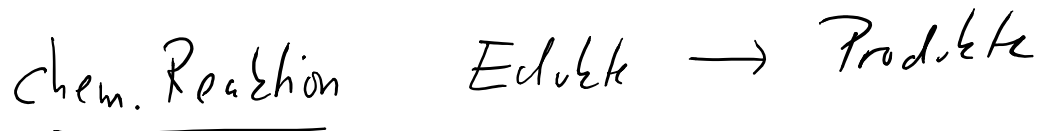
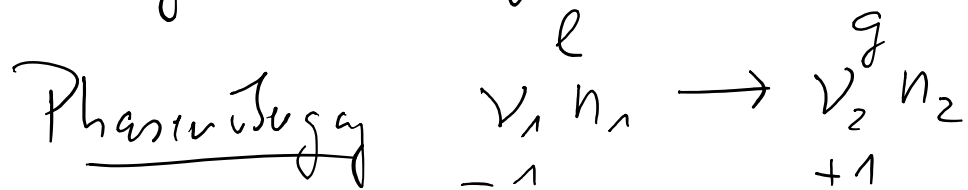
$$\Delta H = \frac{M_{\text{mol}}}{\rho} (1 - T\gamma) \Delta p = 56 \frac{\text{J}}{\text{mol}}$$

Chem. Potential

Bisher : p, T, V, S als Parameter

U, H, A, G als Fktn. von 2 dieser Parameter

Änderung der Stoffmengen dn_1, dn_2, \dots



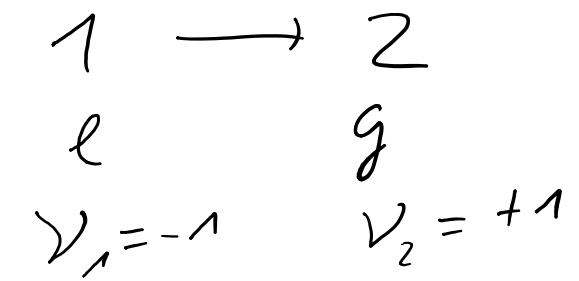
i -Stoffe $v_1 n_1 \dots v_i n_i$

n_1, n_2 :

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p, n_1, n_2} dT + \left(\frac{\partial G}{\partial p} \right)_{T, n_1, n_2} dp + \underbrace{\left(\frac{\partial G}{\partial n_1} \right)_{p, T, n_2}}_{\mu_1} dn_1 + \underbrace{\left(\frac{\partial G}{\partial n_2} \right)_{p, T, n_1}}_{\mu_2} dn_2$$

$\mu_1 \equiv$ Chem. Potential von Stoff 1

Phasenübergang



$$\frac{dn_1}{-1} = \frac{dn_2}{+1} = d\xi$$

P, T konstant

$$dG = \sum_{i=1}^2 \mu_i dn_i = \sum_{i=1}^2 \mu_i \nu_i d\xi$$

$$= \left(\sum_{i=1}^2 \nu_i \mu_i \right) d\xi$$

$$= (\mu_2 - \mu_1) d\xi \quad \begin{array}{l} dG > 0 \\ \mu_2 > \mu_1 \end{array}$$

Reaktionen

$$dG = \sum_i \mu_i dn_i$$

$$\Delta G = \int_1^2 \sum_i \mu_i dn_i$$

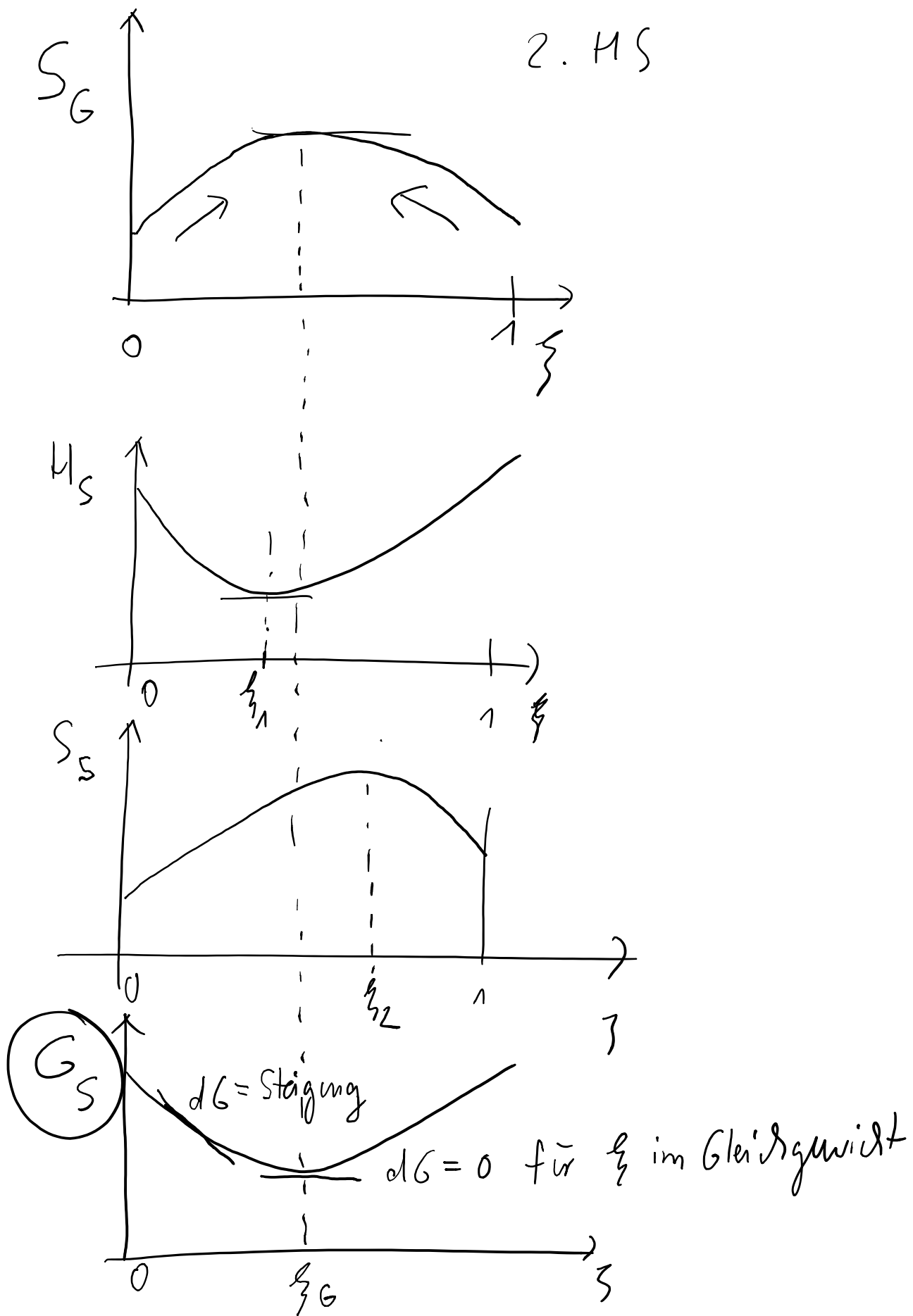
$$= \sum_i \left(\mu_i \int_1^2 dn_i \right)$$

$$= \sum_i \mu_i \left(\overbrace{n_{2i} - n_{1i}}^{\Delta n_i} \right)$$

Stoffabhängigkeit von U, H, A

$$\left(\frac{\partial G}{\partial n_i}\right)_{p,T, \text{ alle } n \neq n_i} \equiv \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n \neq n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{S, p, n \neq n_i} \\ = \left(\frac{\partial A}{\partial n_i}\right)_{V, T, n \neq n_i}$$

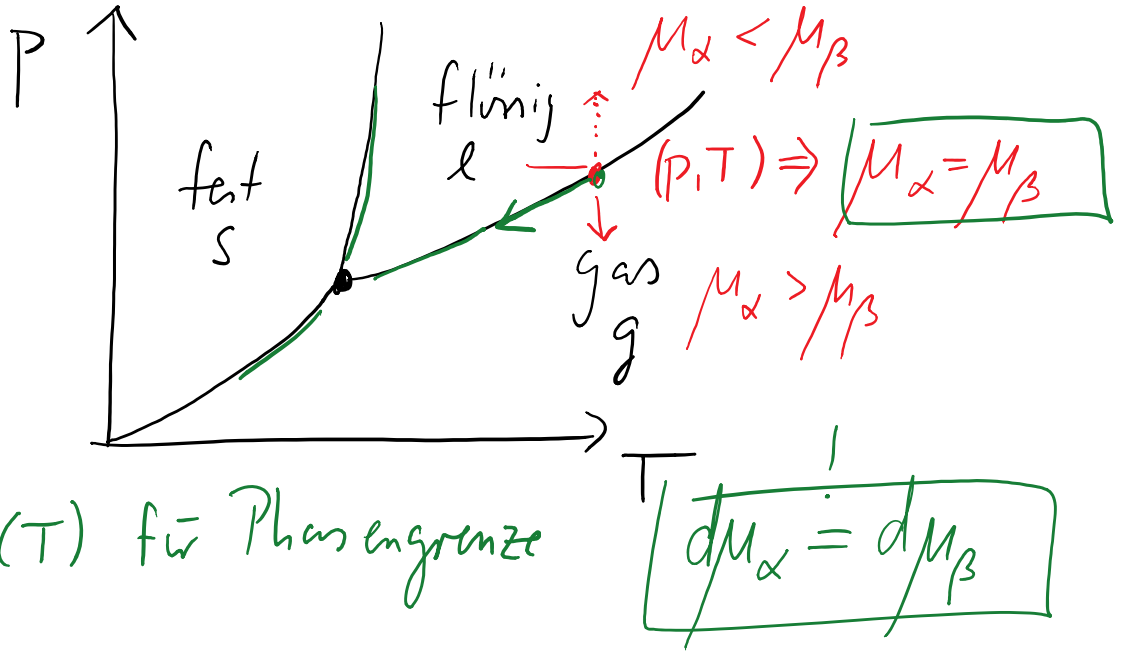
Chem. Gleichgewicht



Phasenübergänge

Mittwoch, 20. Mai 2015 14:07

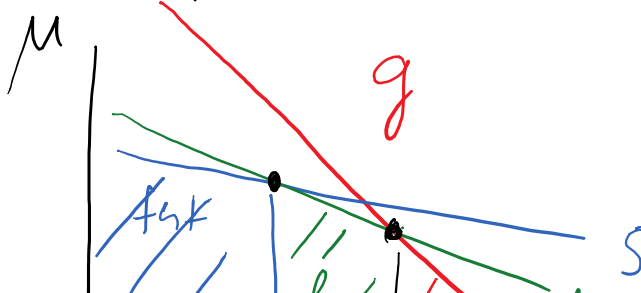
Chemische Potentiale μ_α, μ_β

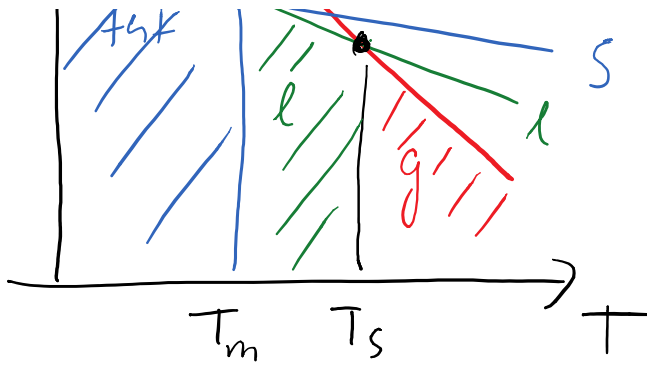


$$\mu = \left(\frac{\partial G}{\partial n} \right) \equiv G^m$$

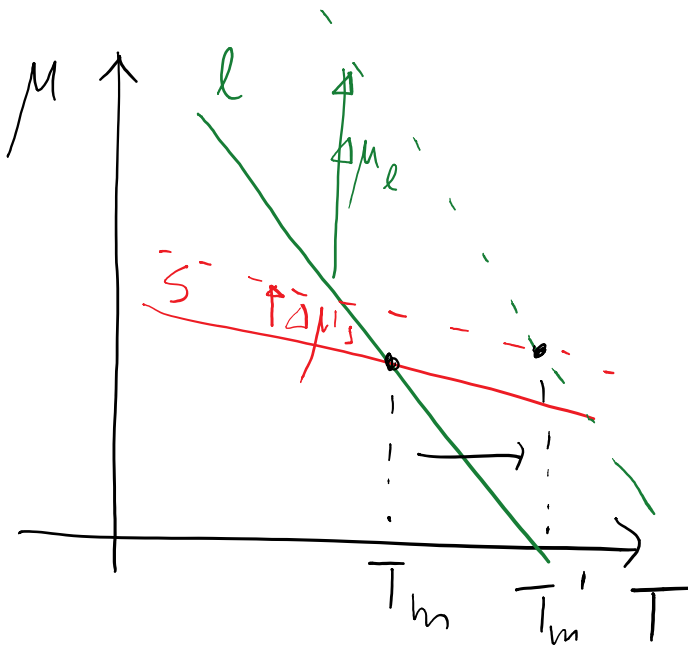
$$d\mu = \underbrace{\left(\frac{\partial \mu}{\partial T} \right)_p}_{-S^m} dT + \underbrace{\left(\frac{\partial \mu}{\partial p} \right)_T}_{V^m} dp$$

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S_m$$





Druckabhängigkeit $\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$



$$V_m(s) < V_m(l) \ll V_m(g)$$

$$\left(\frac{\partial \mu_s}{\partial p}\right)_T < \left(\frac{\partial \mu_l}{\partial p}\right)_T$$

$$\Delta \mu_s < \Delta \mu_l \text{ bei } \Delta p$$

Phasengrenzlinie

$$\underbrace{d\mu_\alpha} = \underbrace{d\mu_\beta} \quad \alpha, \beta \text{ zwei Phasen}$$

$$-S_\alpha^m dT + V_\alpha^m dp = -S_\beta^m dT + V_\beta^m dp$$

$$\underbrace{(S_\beta^m - S_\alpha^m)}_{\Delta S^m} dT = \underbrace{(V_\beta^m - V_\alpha^m)}_{\Delta V^m} dp$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta S^m}{\Delta V^m}}$$

Clausius-Gleichung

$$\Delta S^m = \frac{\Delta H^m}{T}$$

Phasenübergang reversibel

$$\boxed{\frac{dp}{dT} = \frac{\Delta H^m}{T \Delta V^m}}$$

Clausius-Clapeyron
Gleichung

flüssig - gasförmig

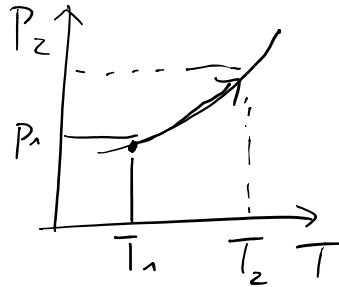
Flüssig α \rightarrow Gasförmig β

$$\Delta V^m = V_{\text{gas}}^m - V_{\text{flüssig}}^m \approx V_{\text{gas}}^m \approx \frac{R \cdot T}{p}$$

$$V_{\text{gas}}^m \approx 1000 \cdot V_{\text{flüssig}}^m$$

$$\frac{dp}{dT} = \frac{\Delta H^m p}{T^2 R}$$

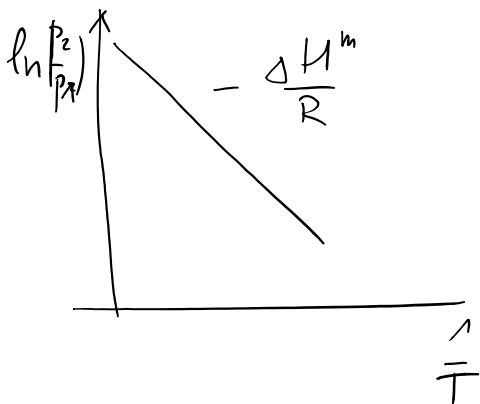
Steigung von $p(T)$



$$\frac{1}{p} dp = \frac{\Delta H^m}{R} \frac{1}{T^2} dT \quad \Delta H^m \neq f(T)$$

$$\int_{p_1}^{p_2} \frac{1}{p} dp = \frac{\Delta H^m}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

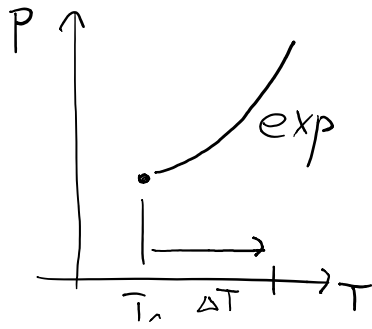
$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H^m}{R} \left(-\frac{1}{T_2} + \frac{1}{T_1}\right) = -\frac{\Delta H^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



$$\frac{p_2}{p_1} = \exp \left\{ -\frac{\Delta H^m}{R} \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) \right\} = \exp \left\{ \frac{\Delta H^m}{R} \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right) \right\}$$

$$\approx \exp \left\{ \frac{\Delta H^m}{R T_1^2} \Delta T \right\}$$

$p \uparrow$,



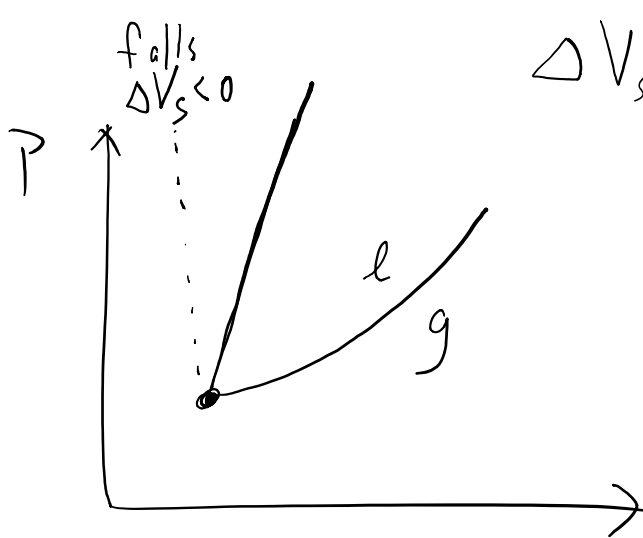
$$\approx \exp \left[\frac{\Delta T}{T_1} \right]$$

mit $\Delta T = T_2 - T_1$

Fest - Flüssig

Phasengrenze fest \rightarrow flüssig
 α β

$$\frac{dp}{dT} = \frac{\Delta H_{\text{schmelz}}^m}{T \Delta V_{\text{schmelz}}^m} \rightarrow$$



$$\Delta V_{\text{schmelz}}^m \ll \Delta V_{\text{verdamp}}^m$$

$$\hookrightarrow \frac{dp}{dT}_{\text{schmelz}} \gg \frac{dp}{dT}_{\text{verdampf}}$$

$$dp = \frac{\Delta H_s^m}{\Delta V_s^m} \cdot \frac{1}{T} dT$$

falls:
 $\Delta H_s^m \neq f(T)$
 $\Delta V_s^m \neq f(T)$

$$\int_{P_1}^{P_2} dp = \frac{\Delta H_s^m}{\Delta V_s^m} \int \frac{1}{T} dT$$

$$P_2 - P_1 = \frac{\Delta H_s^m}{\Delta V_s^m} \cdot \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta H_s^m \cdot \ln\left(\frac{T_2}{T_1}\right)$$

$$\frac{\Delta V_s^m}{\Delta V_s^m} \ln \left(1 + \frac{\Delta T}{T_1} \right)$$

$$\left(\ln(1+x) \approx x \right)$$

$x \ll 1$

$$P_2 - P_1 = \frac{\Delta H_s^m}{\Delta V_s^m} \cdot \frac{\Delta T}{T_1} \quad \underline{\text{Gerade}}$$

$$P_2 = P_1 + \underbrace{\frac{\Delta H_s^m}{\Delta V_s^m T_1}}_{\text{Steigung}} \Delta T$$