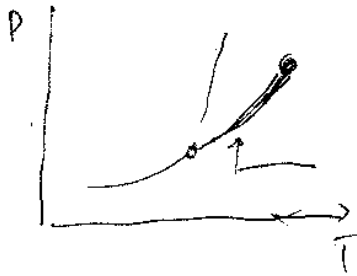


Übungsblatt 9 – Lösungen

A9.1:



$$\ln(p/\text{Torr}) = 16.255 - (25018/T[\text{K}])$$

~~trans~~ - Clapeyron:

$$\frac{dp}{dT} =$$

$$d\mu_\alpha = d\mu_\beta \Rightarrow -S_{m,\alpha}dT + V_{m,\alpha}dp = -S_{m,\beta}dT + V_{m,\beta}dp$$

$$\Rightarrow \Delta S_m(\beta-\alpha) dT = \Delta V_m(\beta-\alpha) dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta S_m(\beta-\alpha)}{\Delta V_m(\beta-\alpha)} \quad (\text{Clapeyron} \approx \text{Cl.})$$

Verdampfung / Dampfdruckkurve: $\beta = \text{Gas}$, $\alpha = \text{flüssig}$.

$$\Delta S_m(l \rightarrow g) = \frac{\Delta H_{v,m}}{T_{\text{sdap}}}$$

$$\frac{dp}{dT} = \frac{\Delta H_{v,m}}{T \cdot \Delta V_m(l \rightarrow g)}$$

$$= \frac{p \Delta H_{v,m}}{RT^2}$$

$$\text{id. Gas: } \Delta V_m(l \rightarrow g) =$$

$$V_m(g) - V_m(l) \approx V_m(g)$$

$$\Rightarrow \Delta V_m(l \rightarrow g) \approx \frac{RT}{p}$$

$$\Rightarrow \frac{dp}{p} = \frac{\Delta H_{v,m}}{RT^2} dT$$

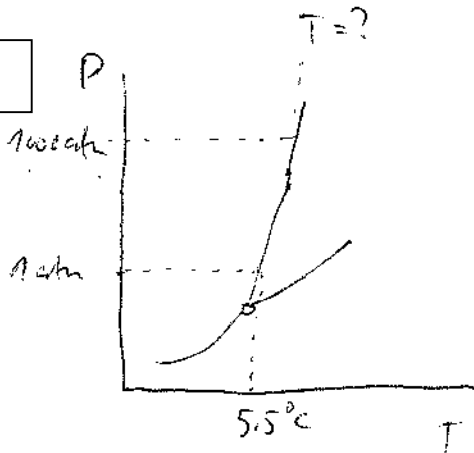
$$d \ln p = \frac{\Delta H_{v, \text{m}}}{RT^2} dT$$

$$\Rightarrow \ln p = \text{const} - \frac{\Delta H_{v, \text{m}}}{RT}$$

$$\Rightarrow \frac{\Delta H_{v, \text{m}}}{R} = 2501.8 [\text{K}]$$

$$\begin{aligned} \Rightarrow \Delta H_{v, \text{m}} &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 2501.8 \text{ K} = \\ &= 20.8 \text{ kJ mol}^{-1} \end{aligned}$$

A9.2:



Schmelzdruckkurve

$$\rho(s) = 0.891 \text{ g cm}^{-3}$$

$$\rho(l) = 0.879 \text{ g cm}^{-3}$$

$$\Delta H_{\text{sm}} = 10.33 \text{ kJ mol}^{-1}$$

(Clausius):

$$\frac{dp}{dT} = \frac{\Delta H_{\text{sm}, \text{m}}}{T_{\text{sup}} \cdot \Delta V_{\text{m}}(s \rightarrow l)}$$

$$\Delta T \approx \frac{T_{\text{sup}} \cdot \Delta V_{\text{m}}(s \rightarrow l)}{\Delta H_{\text{sm}, \text{m}}} \Delta p$$

$$\begin{aligned} \Delta V_{\text{m}} &= M \cdot \rho^{-1} \Rightarrow \Delta V_{\text{m}} = V_{\text{m}}(l) - V_{\text{m}}(s) = \\ &= M \left(\frac{1}{\rho(l)} - \frac{1}{\rho(s)} \right) = \end{aligned}$$

$$\begin{aligned}
 \Rightarrow \Delta T &= \frac{278.65 \text{ K} \cdot 78 \text{ g} \cdot \text{mol}^{-1}}{10.59 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1} \cdot \text{Nm}} \left(\frac{1}{0.879} - \frac{1}{0.847} \right) \cdot 999 \text{ g} \cdot \text{cm}^{-3} \\
 &= \frac{278.65 \text{ K} \cdot 78 \cdot 0.0113 \cdot 999 \cdot 10^5}{10.59 \cdot 10^3} \frac{\text{cm}^3 \cdot \text{K} \cdot \text{N} \cdot 10^6}{\text{Nm} \cdot \text{m}^2 \cdot \text{cm}^3} \\
 &= 3.137 \text{ K}
 \end{aligned}$$

$$T_{\text{sup}}(1000 \text{ atm}) = T_{\text{sup}}(1 \text{ atm}) + 3.14 \text{ K}$$

$$\begin{aligned}
 \Rightarrow T_{\text{sup}}(\text{Bentol}, 1000 \text{ atm}) &= 5.5^\circ\text{C} + 3.14^\circ\text{C} = \\
 &= \underline{\underline{8.64^\circ\text{C}}}
 \end{aligned}$$

flüssig

$$\frac{1}{T} dT = \frac{\Delta V_m(s \rightarrow l)}{\Delta H_{sm}} dp$$

Wie man sieht, macht man nur einen geringfügigen Fehler, wenn man $\ln(T/T^*)$ durch $(T-T^*)/T^*$ ersetzt. (Achtung: T-Abh. von ΔH und ΔV wurde in beiden Fällen vernachlässigt)

$$\int_{T_1}^{T_2} \frac{1}{T} dT = \frac{\Delta H_{sm}}{\Delta H_{sm}} \int_{p_1}^{p_2} dp$$

$$\Rightarrow \ln \frac{T_2}{T_1} = \frac{\Delta V_m(s \rightarrow l)}{\Delta H_{sm}} \Delta p$$

$$\Rightarrow \ln T_2 = \ln T_1 + \frac{\Delta V_m}{\Delta H_{sm}} \Delta p$$

$$T_2 = T_1 \cdot e^{+\frac{\Delta V_m}{\Delta H_{sm}} \Delta p} = T_1 e^x$$

$$x = \frac{78 \text{ g} \cdot \left(\frac{1}{0.873} - \frac{1}{0.891} \right) \cdot 999}{10.55 \cdot 10^3 \cdot 10}$$

$$\frac{9 \cdot \text{cm}^3 \cdot 10^{-6} \text{ m}^3 \cdot 10^5 \text{ N} \cdot \text{m}^{-2}}{\text{mol} \cdot 9 \cdot \text{cm}^3 \cdot 10^3 \cdot \text{m}^2 \cdot \text{N} \cdot \text{m}^{-2}}$$

$$= 0.0113$$

$$e^x = 1.0113$$

$$\Rightarrow T_2 = 278.65 \text{ K} \cdot 1.0113 = 281.80 \text{ K} \hat{=} \underline{\underline{8.655^\circ \text{C}}}$$

Clausius-Clapeyron:

$$d \ln p = \frac{\Delta H_{v,m}}{RT^2} dT$$

$$a) \quad \ln \frac{p_2}{p_1} = \frac{\Delta H_{v,m}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta H_{v,m} = \frac{R \ln p_2/p_1}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \cdot \ln \frac{40}{10}}{\frac{1}{359} - \frac{1}{392.5}} \quad \frac{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{\text{K}^{-1}}$$

$$= 48,48 \text{ kJ mol}^{-1}$$

$$b) \quad \text{Standard statepunkt: } T_{\text{sdp}}^* (760 \text{ Torr})$$

$$\ln \frac{p^*}{p_2} = \frac{\Delta H_{v,m}}{R} \left(\frac{1}{T_2} - \frac{1}{T^*} \right)$$

$$\Rightarrow \frac{1}{T^*} = \frac{1}{T_2} - \frac{R}{\Delta H_{v,m}} \ln \frac{p^*}{p} = \frac{1}{392.5 \text{ K}} - \frac{8.314 \text{ J mol}^{-1}}{48480 \text{ kJ mol}^{-1}} \ln \frac{760}{40} =$$

$$= \frac{1}{392.5 \text{ K}} - \frac{1}{1980.4} = 7.043 \cdot 10^{-3}$$

$$\Rightarrow T^* = 489.5 \text{ K} \approx 216.37^\circ \text{C} \quad (\text{konkret Wert } 218^\circ \text{C})$$

$$c) \quad \Delta S_{v,m}^* = \frac{\Delta H_{v,m}}{T^*} = \frac{48480 \text{ J mol}^{-1}}{489.5 \text{ K}^{-1}} = 99.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

A9.4:

Ideale Mischung, da Wechselwirkungen sehr ähnlich, da Moleküle sehr ähnlich

Mischungsentropie: $\Delta S_{\text{mix}} = nR(x_A \ln x_A + x_B \ln x_B) =$

$$nR(x_A \ln x_A + (1-x_A) \ln(1-x_A))$$

Maximierungsbedingung: $\frac{\partial \Delta S_{\text{mix}}}{\partial x_A} = nR(\ln x_A + 1 - \ln(1-x_A) + (1-x_A) \cdot \left(\frac{1}{1-x_A}\right) \cdot (-1)) =$

$$= nR(\ln x_A + 1 - \ln(1-x_A) - 1) =$$

$$= nR \ln \frac{x_A}{1-x_A} = 0$$

$$\Rightarrow \ln 1 = 0 \Rightarrow \frac{x_A}{1-x_A} = 1$$

$$\Rightarrow x_A = 1-x_A \Rightarrow 2x_A = 1$$

$$\Rightarrow x_A = \frac{1}{2}$$

$$\Rightarrow a) \frac{w_{\text{Hex}}}{w_{\text{HeP}}} = 1 = \frac{m_{\text{Hex}} / M_{\text{Hex}}}{m_{\text{HeP}} / M_{\text{HeP}}} = \frac{w_{\text{Hex}}}{w_{\text{HeP}}} \cdot \frac{M_{\text{HeP}}}{M_{\text{Hex}}}$$

$$\Rightarrow b) \frac{w_{\text{Hex}}}{w_{\text{HeP}}} = \frac{M_{\text{Hex}}}{M_{\text{HeP}}} = \frac{86}{100} = 0.86$$