

1. We have a cylinder with a piston, which is adiabatically isolated and keeps 30 *bar* constant pressure. At start it has 1000 *mol* liquid water in it at its boiling point, and the same amount of steam at 380 °C temperature.
  - a ) Consider the gas to be real. Illustrate the process in which the system reaches equilibrium on a T-s diagram! Determine the equilibrium temperature, and the change in enthalpy and entropy.
  - b ) Consider the gas to be ideal. Determine the same values as in a)! The heat of vaporization is 1800 kJ/kg, the average specific heat capacity of the steam is 2,67 kJ/kgK. Read the boiling point temperature from the T-s diagram.

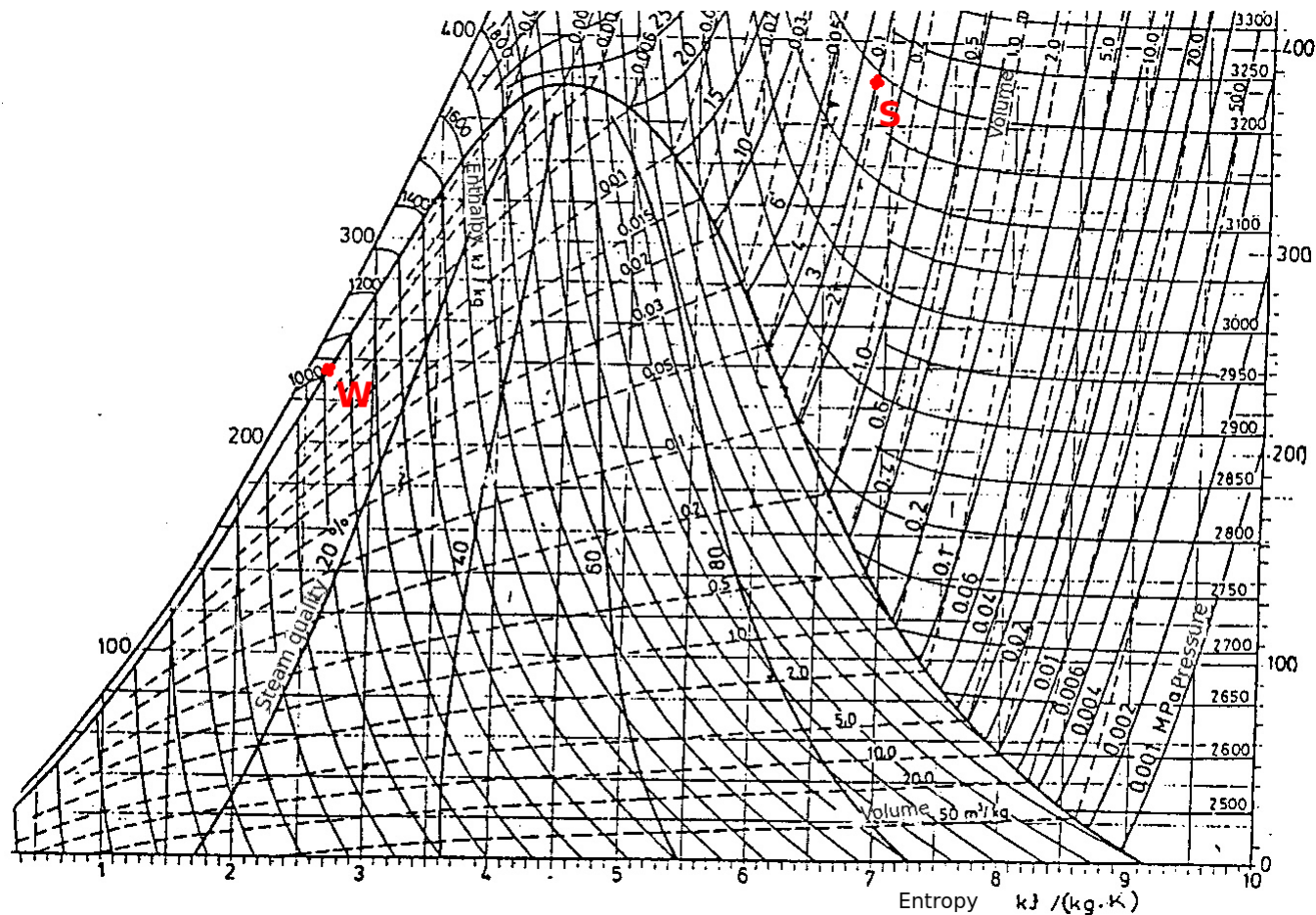
**(8 points)**

$$Q = 0 \quad J = Q_{steam} + Q_{water}$$

$$= Q_{380^{\circ}C \rightarrow T_{eq}} + Q_{water \rightarrow steam} \quad ( + Q_{T_{boil} \rightarrow T_{eq}} ? )$$

a ) Steam subsystem: crossing of  $380^{\circ}C$  and  $3 \text{ MPa}$

Water subsystem: crossing of  $3 \text{ MPa}$  and left side of the bell curve



$$Q_{steam, 380^{\circ}C \rightarrow T_{boil}} = m \cdot \Delta h = 18 \text{ kg} \cdot (2800 - 3190) \frac{\text{kJ}}{\text{kg}}$$

$$= -7020 \text{ kJ}$$

$$Q_{water \rightarrow steam} = m \cdot T_{boil} \cdot \Delta s$$

$$= 18 \text{ kg} \cdot 508 \text{ K} \cdot (6,2 - 2,7) \frac{\text{kJ}}{\text{kgK}} = 32000 \text{ kJ}$$

$|Q_{steam, 380^{\circ}C \rightarrow T_{boil}}| < |Q_{water \rightarrow steam}| \rightarrow$  not enough heat in the steam to evaporate all the water  $\rightarrow T_{eq} = 235^{\circ}C$

$$\Delta s_{steam} = (6,2 - 6,9) \frac{\text{kJ}}{\text{kgK}} = -0,7 \frac{\text{kJ}}{\text{kgK}}$$

$$\Delta s_{water} = \frac{-Q_{steam, 380^{\circ}C \rightarrow T_{boil}}}{T_{boil} \cdot m} = \frac{7020 \text{ kJ}}{18 \text{ kg} \cdot 508 \text{ K}} = 0,77 \frac{\text{kJ}}{\text{kgK}}$$

$$\Delta S = 18 \text{ kg} \cdot 0,77 \frac{\text{kJ}}{\text{kgK}} - 18 \text{ kg} \cdot 0,7 \frac{\text{kJ}}{\text{kgK}} = 1,26 \frac{\text{kJ}}{\text{K}}$$

How much of the water subsystem became steam?

$(2,7 + 0,77) \frac{\text{kJ}}{\text{kgK}} \approx 3,5 \frac{\text{kJ}}{\text{kgK}}$ : belongs to about 22% steam quality

Final system:  $\frac{18 \text{ kg} \cdot 0,22 + 18 \text{ kg} \cdot 1}{36 \text{ kg}} = 0,61 \rightarrow 61\%$  steam quality

$\Delta H = 0 J$ : adiabatic, isobaric processes

b ) We have to check if the same processes happen with an ideal gas steam

$$Q_{steam, 380^\circ C \rightarrow T_{boil}} = m \cdot c_p \cdot \Delta T = 18 \text{ kg} \cdot 2,67 \frac{\text{kJ}}{\text{kgK}} \cdot (-145 \text{ K}) = -6969 \text{ kJ}$$

$$Q_{water \rightarrow steam} = m \cdot \lambda_v = 18 \text{ kg} \cdot 1800 \frac{\text{kJ}}{\text{kg}} = 32400 \text{ kJ}$$

Same situation as before

$$\Delta H = 0 J$$

$$\Delta S = \frac{6969 \text{ kJ}}{508 \text{ K}} + 18 \text{ kg} \cdot 2,67 \frac{\text{kJ}}{\text{kgK}} \cdot \ln \frac{508 \text{ K}}{653 \text{ K}} = 1,65 \frac{\text{kJ}}{\text{K}}$$

How much of the water evaporated?

$$\Delta m_{water} = -\frac{6969 \text{ kJ}}{1800 \frac{\text{kJ}}{\text{kg}}} = -3,87 \text{ kg}$$

$$\frac{3,87 \text{ kg} + 18 \text{ kg}}{36 \text{ kg}} = 0,6075 \rightarrow 60,75\% \text{ steam quality}$$

2. Estimate the equilibrium vapor pressure of toluene at  $75\text{ }^{\circ}\text{C}$ , if its boiling point temperature at standard pressure is  $110\text{ }^{\circ}\text{C}$ , and the latent heat of vaporization for toluene is  $38,1\text{ kJ/mol}$ !

**(4 points)**

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Boiling point at standard pressure is  $110\text{ }^{\circ}\text{C} \rightarrow$  eq. vapor pressure at  $110\text{ }^{\circ}\text{C}$  is the standard pressure ( $1\text{ bar}$ )

$$p^*(75^{\circ}\text{C}) = ?$$

$$\text{Clausius-Clapeyron: } \ln \frac{p^*(110^{\circ}\text{C})}{p^*(75^{\circ}\text{C})} = -\frac{\lambda}{R} \cdot \left( \frac{1}{383\text{ K}} - \frac{1}{348\text{ K}} \right)$$

$$p^*(75^{\circ}\text{C}) = \frac{1\text{ bar}}{e^{-\frac{38100\text{ J/mol}}{R} \cdot \left( \frac{1}{383\text{ K}} - \frac{1}{348\text{ K}} \right)}} = 0,3017\text{ bar}$$

3. We have a closed system consisting of  $25^{\circ}\text{C}$ ,  $5 \text{ mol}$   $n$ -heptane –  $n$ -hexane mixture in which the molar fraction of  $n$ -heptane is 0,4. How many  $\text{mols}$  of substance will be in vapor phase if we set the pressure to  $9 \text{ kPa}$ ? The equilibrium vapor pressure of  $n$ -hexane at  $25^{\circ}\text{C}$  is  $13 \text{ kPa}$ , and  $5,2 \text{ kPa}$  for  $n$ -heptane.

For what molar fractions is an  $n$ -heptane –  $n$ -hexane mixture in two phases at  $25^{\circ}\text{C}$  temperature and at  $10 \text{ kPa}$  pressure?

**(7 points)**

$$n = 5 \text{ mol}, z_{hept} = 0,4$$

$$n_g = ?$$

$$n = n_g + n_l$$

$$\frac{n_g}{n_l} = \frac{n_g}{5 \text{ mol} - n_g} = \frac{x_{hex} - z_{hex}}{z_{hex} - y_{hex}}$$

$$z_{hex} = 1 - z_{hept} = 0,6$$

Dalton's law:  $p = p_{hept}^* \cdot (1 - x_{hex}) + p_{hex}^* \cdot x_{hex}$

$$\rightarrow x_{hex} = \frac{p - p_{hept}^*}{p_{hex}^* - p_{hept}^*} = 0,4872$$

$$y_{hex} = \frac{p_{hex}}{p} = \frac{p_{hex}^* \cdot x_{hex}}{p} = 0,7037$$

$$\frac{n_g}{5 \text{ mol} - n_g} = \frac{0,4872 - 0,6}{0,6 - 0,7037} = 1,0878$$

$$n_g = 2,605 \text{ mol}$$

Lowest  $z_{hex}$  where the system is in two phase is where  $z_{hex} = x_{hex}$

Highest  $z_{hex}$  where the system is in two phase is where  $z_{hex} = y_{hex}$

We have to calculate  $x_{hex}$  and  $y_{hex}$  for 10 kPa

$$x_{hex} = \frac{10 \text{ kPa} - 5,2 \text{ kPa}}{13 \text{ kPa} - 5,2 \text{ kPa}} = 0,6153$$

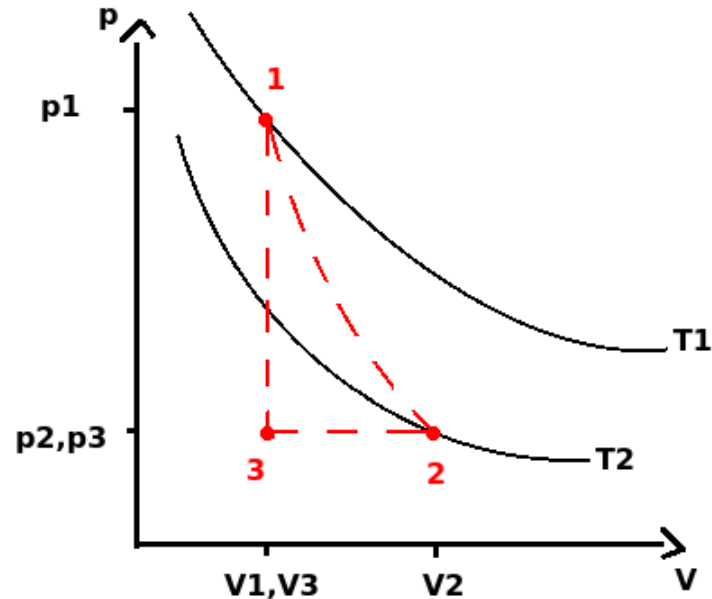
$$y_{hex} = \frac{13 \text{ kPa} \cdot 0,6153}{10 \text{ kPa}} = 0,7999$$

So the system is in two phases at 25 °C and  $p = 10 \text{ kPa}$  if

$$0,6153 \leq z_{hex} \leq 0,7999$$

4. We expand a 5 mol, 520 K, 2 MPa hydrogen gas in adiabatic circumstances to 6 bar. After this we perform an isobaric, and then an isochor process, after which the gas returns to its original state. Illustrate the processes on a p-V diagram! Determine the missing temperature and pressure values! Calculate the heat, work, change in entropy and change in internal energy for each step and for the complete process, and give them in tabular form! The molar heat capacity of hydrogen at constant volume is  $20,54 \text{ J/molK}$ .

**(9 points)**





$$n = 5 \text{ mol}, c_{m,v} = 20,54 \frac{J}{\text{molK}}$$

$$p_1 = 2 \text{ MPa}, T_1 = 520 \text{ K}$$

$$p_2 = 6 \text{ bar}$$

Missing pressure value: none,  $p_3 = p_2$

$$\text{Missing temperature value: } T_2 = T_1 \cdot \left( \frac{p_2}{p_1} \right)^{-\frac{1-\kappa}{\kappa}}$$

$$\text{We need } \kappa = \frac{c_{m,p}}{c_{m,v}}$$

$$c_{m,p} = c_{m,v} + R = 28,854 \frac{J}{\text{molK}}$$

$$\kappa = 1,405 \rightarrow T_2 = 367,5 \text{ K}$$

$T_3$ : Easier to calculate from the isochor relation

$$T_3 = T_1 \cdot \frac{p_3}{p_1} = 156 \text{ K}$$

Adiabatic reversible:

$$Q = 0 \text{ J}, \Delta S = 0 \frac{\text{J}}{\text{K}}$$

$$\Delta U = W = n \cdot c_{m,v} \cdot \Delta T_{1 \rightarrow 2} = 5 \text{ mol} \cdot 20,54 \frac{\text{J}}{\text{molK}} \cdot (-152,5 \text{ K})$$

Isobaric:

$$Q = n \cdot c_{m,p} \cdot \Delta T_{2 \rightarrow 3} = 5 \text{ mol} \cdot 28,854 \frac{\text{J}}{\text{molK}} \cdot (-211,5 \text{ K})$$

$$W = -n \cdot R \cdot \Delta T_{2 \rightarrow 3} = 5 \text{ mol} \cdot R \cdot (-211,5 \text{ K})$$

$$\Delta S = n \cdot c_{m,p} \cdot \ln \frac{T_3}{T_2} = 5 \text{ mol} \cdot 28,854 \frac{\text{J}}{\text{molK}} \cdot \ln \frac{156 \text{ K}}{367,5 \text{ K}}$$

$$\Delta U = n \cdot c_{m,v} \cdot \Delta T_{2 \rightarrow 3} = 5 \text{ mol} \cdot 20,54 \frac{\text{J}}{\text{molK}} \cdot (-211,5 \text{ K})$$

Isochor:

$$W = 0 \text{ J}$$

$$Q = \Delta U = n \cdot c_{m,v} \cdot \Delta T_{3 \rightarrow 1} = 5 \text{ mol} \cdot 20,54 \frac{\text{J}}{\text{molK}} \cdot 364 \text{ K}$$

$$\Delta S = n \cdot c_{m,v} \cdot \ln \frac{T_1}{T_3} = 5 \text{ mol} \cdot 20,54 \frac{\text{J}}{\text{molK}} \cdot \ln \frac{520 \text{ K}}{156 \text{ K}}$$

	$Q(\text{kJ})$	$W(\text{kJ})$	$\Delta S\left(\frac{\text{J}}{\text{K}}\right)$	$\Delta U(\text{kJ})$
$1 \rightarrow 2$	0	-15,7	0	-15,7
$2 \rightarrow 3$	-30,5	8,8	-123,6	-21,7
$3 \rightarrow 1$	37,4	0	123,6	37,4
$\Sigma$	6,9	-6,9	0	0

5. We put a  $250\text{ }^{\circ}\text{C}$  metal plate weighting  $25\text{ g}$  into  $10\text{ g}$  toluene with  $90\text{ }^{\circ}\text{C}$  temperature. The system is adiabatically isolated and keeps constant pressure. What is the equilibrium state (phases, temperature) ? What is the entropy change during the process?

The boiling point of toluene is  $110\text{ }^{\circ}\text{C}$ , its specific heat capacity is  $1,68\frac{\text{kJ}}{\text{kgK}}$ , its heat of evaporation is  $356\frac{\text{kJ}}{\text{kg}}$ . The specific heat capacity of the metal plate is  $0,46\frac{\text{kJ}}{\text{kgK}}$ .

**(7 points)**

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Can the metal give off enough heat to heat the toluene up to  $110\text{ }^{\circ}\text{C}$  ? If yes, can it evaporate all of it?

$$Q_{metal,250^{\circ}C \rightarrow 110^{\circ}C} = 0,025 \text{ kg} \cdot 0,46 \frac{\text{kJ}}{\text{kgK}} \cdot (-140 \text{ K})$$
$$= -1,61 \text{ kJ}$$

$$Q_{toluene,90^{\circ}C \rightarrow 110^{\circ}C} = 0,01 \text{ kg} \cdot 1,68 \frac{\text{kJ}}{\text{kgK}} \cdot 20 \text{ K}$$
$$= 0,336 \text{ kJ}$$

$$|Q_{metal,250^{\circ}C \rightarrow 110^{\circ}C}| > |Q_{toluene,90^{\circ}C \rightarrow 110^{\circ}C}|$$

→ the metal can heat up the toluene to 110 °C

Remaining heat the metal can give while cooling down to 110 °C : 1,61 kJ – 0,336 kJ = 1,274 kJ

$$Q_{toluene,liq. \rightarrow vap.} = 0,01 \text{ kg} \cdot 356 \frac{\text{kJ}}{\text{kg}} = 3,56 \text{ kJ}$$

$Q_{toluene,liq. \rightarrow vap.} > 1,274 \text{ kJ}$  → the metal can't give enough heat to evaporate all the toluene →  $T_{eq} = 110^{\circ}C$

The equilibrium system will be  $110\text{ }^{\circ}\text{C}$ , and it will consist of solid metal, liquid toluene, and gaseous toluene

How much toluene evaporated?  $\frac{1,274\text{ kJ}}{336\frac{\text{kJ}}{\text{kg}}} = 0,0038\text{ kg}$

$\Delta S =$

$$\Delta S_{\text{toluene},90^{\circ}\text{C}\rightarrow 110^{\circ}\text{C}} \quad (0,01\text{ kg} \cdot 1,68\frac{\text{kJ}}{\text{kgK}} \cdot \ln\frac{383\text{ K}}{363\text{ K}})$$

$$+\Delta S_{\text{toluene},\text{liq.}\rightarrow\text{vap.}} \quad \left(\frac{1,274\text{ kJ}}{383\text{ K}}\right)$$

$$+\Delta S_{\text{metal},250^{\circ}\text{C}\rightarrow 110^{\circ}\text{C}} \quad (0,025\text{ kg} \cdot 0,46\frac{\text{kJ}}{\text{kgK}} \cdot \ln\frac{383\text{ K}}{523\text{ K}})$$

$$= 0,6446\frac{\text{J}}{\text{K}}$$

6. We put 10 *mol* benzene-toluene mixture, with 65% benzene, into a cylinder with piston. At 20 °C we set the pressure so that the molar fraction of benzene in the vapor phase is 0,7. What is the volume of the vapor phase if we neglect the volume of the liquid and we treat the vapor as an ideal gas? How much do we need to increase the pressure for the vapor phase to disappear?

The eq. vapor pressure of benzene and toluene at 20 °C is 9960 Pa and 2973 Pa, respectively.

**(8 points)**

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The vapor is ideal gas → we can calculate its volume from  $n_g, R, T$  and  $p$ , but we don't know  $p$  and  $n_g$

Pressure using Raoult's law:

$$p = p_{benz}^* \cdot x_{benz} + p_{tolu}^* \cdot (1 - x_{benz})$$

Pressure using Dalton's law:

$$p = \frac{p_{benz}}{y_{benz}} = \frac{p_{benz}^* \cdot x_{benz}}{y_{benz}}$$

From these two equations we can express  $x_{benz}$ , then we can calculate the pressure

$$\frac{p_{benz}^* \cdot x_{benz}}{y_{benz}} = p_{tolu}^* + (p_{benz}^* - p_{tolu}^*) \cdot x_{benz}$$

$$\rightarrow x_{benz} = \frac{p_{tolu}^*}{\frac{p_{benz}^*}{y_{benz}} - (p_{benz}^* - p_{tolu}^*)} = 0,4106 \rightarrow p = 5842 \text{ Pa}$$

$$n_g = \frac{n_{benz} - n \cdot x_{benz}}{y_{benz} - x_{benz}} = \frac{0,65 \cdot 10 \text{ mol} - 10 \text{ mol} \cdot 0,4106}{0,7 - 0,4106} = 8,2723 \text{ mol}$$

$$V = \frac{n_g \cdot R \cdot T}{p} = 3,45 \text{ m}^3$$



The vapor phase disappears if  $z_{benz} = 0,65 = x_{benz}$

Pressure using Raoult's law:

$$\begin{aligned} p &= p_{benz}^* \cdot x_{benz} + p_{tolu}^* \cdot (1 - x_{benz}) \\ &= 9960 \text{ Pa} \cdot 0,65 + 2973 \text{ Pa} \cdot 0,35 = 7515 \text{ Pa} \end{aligned}$$