

# Physical Chemistry I. practice

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III.: Thermal equilibrium & real gases

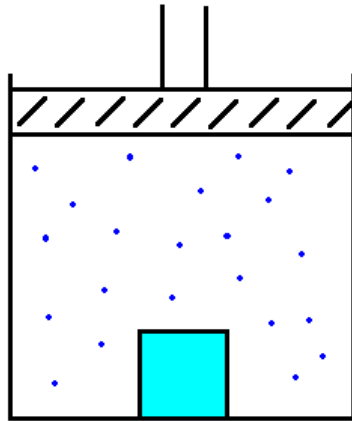
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# Thermal equilibrium

We have a system of 90 g, 0 °C ice and 18 g, 100 °C water vapor. The system reaches equilibrium without exchanging heat with the environment (adiabatic) and at constant pressure (1 bar). What are the equilibrium  $T$  and the total  $\Delta S$  ?



$$\lambda_v = 41,4 \text{ kJ/mol}$$

$$\lambda_f = 6,02 \text{ kJ/mol}$$

$$C_m = 75,312 \text{ J/(mol K)}$$

# Thermal equilibrium

0th step: What processes will take place?

Melting of ice:  $5 \text{ mol} \cdot 6,02 \text{ kJ/mol} = \underline{30,1 \text{ kJ}}$

Condensation of vapor:  $1 \text{ mol} \cdot \underline{-41,4 \text{ kJ/mol}}$

→ There remains some vapor after all of the ice melted

Heating up the water from the ice from  $0 \text{ }^\circ\text{C}$  to  $100 \text{ }^\circ\text{C}$ :

$5 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot (373 \text{ K} - 273 \text{ K}) = \underline{37,656 \text{ kJ}}$

Condensation of remaining vapor:  $(-41,4 \text{ kJ} + 30,1 \text{ kJ}) = \underline{-11,3 \text{ kJ}}$

→ Not enough to heat the liquid to  $100 \text{ }^\circ\text{C}$

→ The condensed vapor will cool further and the melted ice warm further

→ Equilibrium system is liquid water with  $0 \text{ }^\circ\text{C} < T_{eq} < 100 \text{ }^\circ\text{C}$

# Thermal equilibrium

Adiabatic system:  $Q = 0 \quad J = Q_{\text{ice}} + Q_{\text{vapor}}$

$$Q_{\text{ice}} = n_{\text{ice}} \cdot \lambda_f + n_{\text{ice}} \cdot C_m \cdot (T_{\text{eq}} - 273 \text{ K})$$

$$Q_{\text{vapor}} = -n_{\text{vapor}} \cdot \lambda_v + n_{\text{vapor}} \cdot C_m \cdot (T_{\text{eq}} - 373 \text{ K})$$

$$0 = 5 \text{ mol} \cdot 6,02 \cdot 10^3 \text{ J/mol}$$

$$+5 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot (T_{\text{eq}} - 273 \text{ K})$$

$$-1 \text{ mol} \cdot 41,4 \cdot 10^3 \text{ J/mol}$$

$$+1 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot (373 \text{ K} - T_{\text{eq}})$$

$$\rightarrow T_{\text{eq}} = 314,7 \text{ K} = 41,7 \text{ }^\circ\text{C}$$

# Thermal equilibrium

Change in entropy?  $dS = \frac{\delta Q}{T}$

Phase change:  $\Delta S = \frac{\Delta H_{p.c.}}{T_{p.c.}} = \frac{n \cdot \lambda}{T_{p.c.}}$

Heating / cooling:  $\Delta S = \int_{T_1}^{T_2} \frac{n \cdot C_m}{T} \cdot dT = n \cdot C_m \cdot \ln \frac{T_2}{T_1}$

Melting of ice:  $\Delta S_{\text{ice} \rightarrow \text{liq.}} = \frac{5 \text{ mol} \cdot 6,02 \cdot 10^3 \text{ J/mol}}{273 \text{ K}}$

Heating of liquid from the ice:

$\Delta S_{\text{liq.} 0^\circ\text{C} \rightarrow \text{liq.} 41,7^\circ\text{C}} = 5 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot \ln \frac{314,7 \text{ K}}{273 \text{ K}}$

Condensation of vapor:  $\Delta S_{\text{vap.} \rightarrow \text{liq.}} = \frac{1 \text{ mol} \cdot (-41,4 \cdot 10^3 \text{ J/mol})}{373 \text{ K}}$

Cooling of liquid from the vapor:

$\Delta S_{\text{liq.} 100^\circ\text{C} \rightarrow \text{liq.} 41,7^\circ\text{C}} = 1 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot \ln \frac{314,7 \text{ K}}{373 \text{ K}}$

# Thermal equilibrium

$$\sum \Delta S = 40 \text{ J/K}$$

What if we have  $n_{\text{vapor}} = 0,01 \text{ mol}$  and  $n_{\text{ice}} = 5 \text{ mol}$  ?

(1 bar, adiabatic,  $T_{\text{ice}} = 0 \text{ }^\circ\text{C}$ ,  $T_{\text{vapor}} = 100 \text{ }^\circ\text{C}$ )

Condensation of vapor:  $0,01 \text{ mol} \cdot (-41,4 \cdot 10^3 \text{ J/mol}) = \underline{\underline{-414 \text{ J}}}$

Cooling of liquid from vapor to  $0 \text{ }^\circ\text{C}$ :

$$0,01 \text{ mol} \cdot 75,312 \text{ J/(mol K)} \cdot (273 \text{ K} - 373 \text{ K}) \approx \underline{\underline{-75 \text{ J}}}$$

Melting of ice:  $30100 \text{ J} \rightarrow$  Not all ice will melt!

Equilibrium:  $0 \text{ }^\circ\text{C}$ , ice/liquid system

How much of the ice melts?  $\Delta S = ?$

# Thermal equilibrium

$$Q = 0 \quad J = Q_{\text{ice}} + Q_{\text{vapor}}; \quad \Delta T_{\text{vap.}} = -100 \text{ K}$$

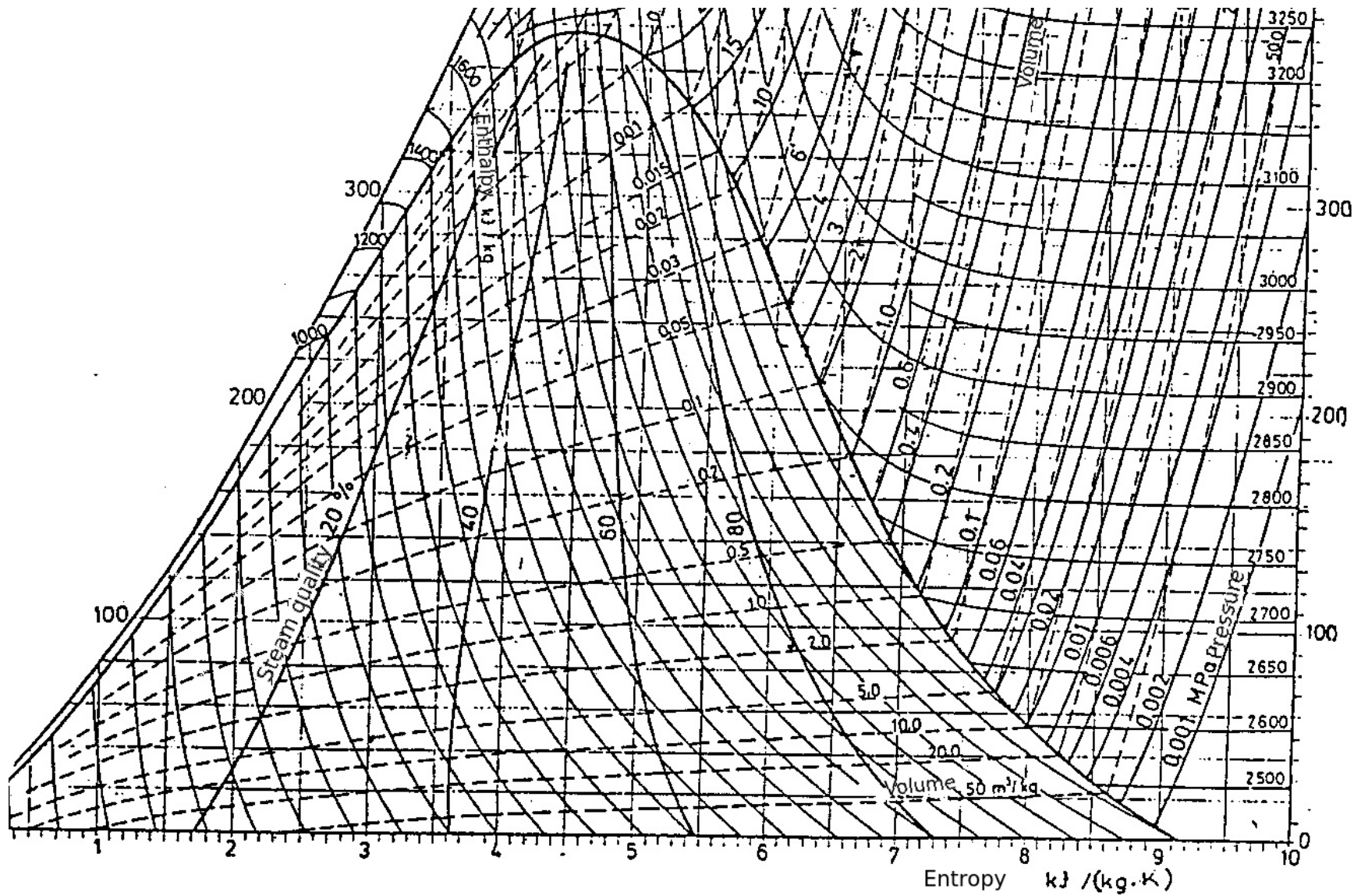
$$\Delta n_{\text{ice}} \cdot \lambda_f - n_{\text{vap.}} \cdot \lambda_v + C_m \cdot n_{\text{vap.}} \cdot \Delta T_{\text{vap.}} = 0 \text{ J}$$

$$\rightarrow \Delta n_{\text{ice}} = 0,08 \text{ mol}$$

$$\Delta S = \frac{\Delta n_{\text{ice}} \cdot \lambda_f}{T_{\text{melt.}}} - \frac{n_{\text{vap.}} \cdot \lambda_v}{T_{\text{boil.}}} + C_m \cdot n_{\text{vap.}} \cdot \ln \frac{T_{\text{melt.}}}{T_{\text{boil.}}}$$

$$\rightarrow \Delta S = 0,419 \text{ J/K}$$

# Real systems: water T-s diagram





# Real systems: water T-s diagram

$$\Delta U = m \cdot \Delta u = W + Q = m \cdot [\Delta h - \Delta(pv)]$$

Isochor:  $\Delta V = 0$

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

$$Q = m \cdot \Delta u = m \cdot (\Delta h - v\Delta p)$$

Isobaric:  $\Delta p = 0$

$$W = -m \cdot p \cdot \Delta v$$

$$Q = m \cdot \Delta h$$

Isothermal:  $\Delta T = 0$

$$Q = m \cdot T \cdot \Delta s$$

$$W = \Delta U - Q$$

Adiabatic reversible:  $\Delta S = 0$

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

$$W = \Delta U$$

Adiabatic throttle:  $\Delta H = 0$

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

$$W = \Delta U = -m \cdot \Delta(pv)$$

Ideal compressor:  $W = \Delta H$

$$W = m \cdot \Delta h$$

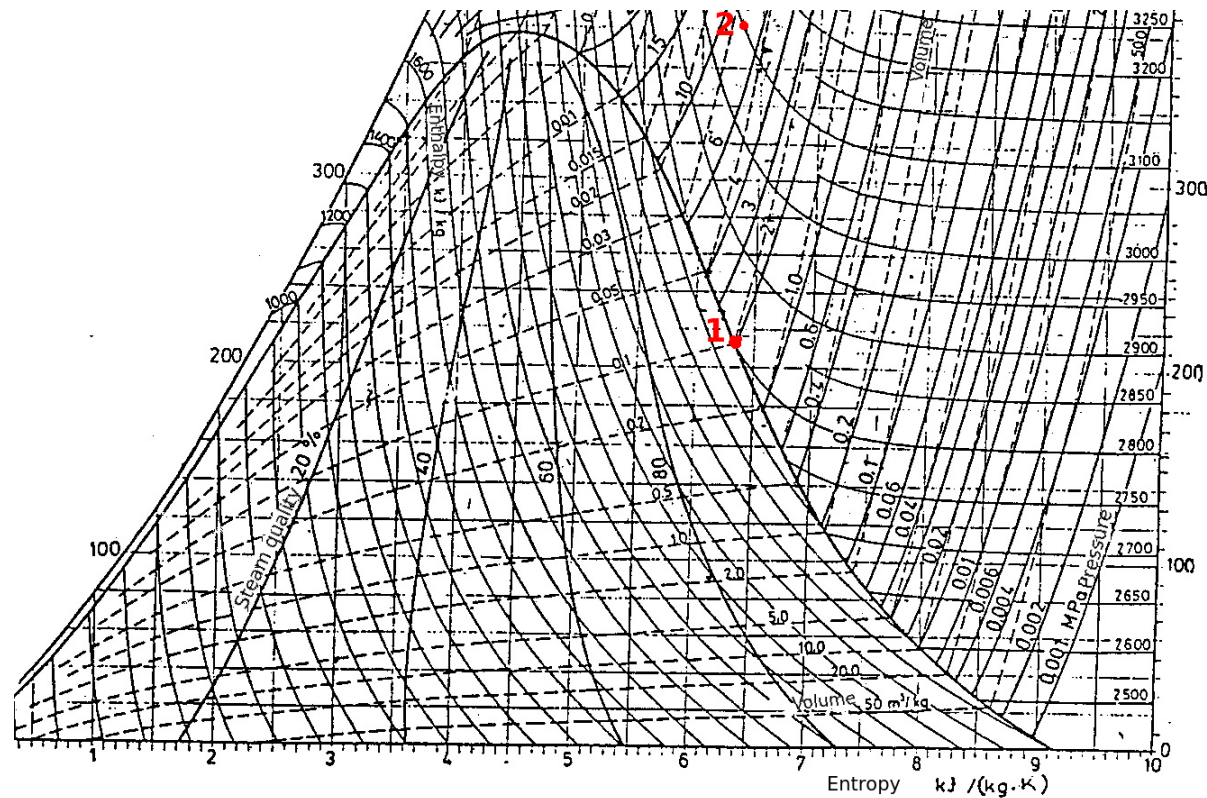
$$Q = \Delta U - W = -m \cdot \Delta(pv)$$

# Real systems: adiabatic reversible

We have 1 kg saturated water vapor in a cylinder with a piston.

In an adiabatic reversible process we compress it from 2 MPa to 8 MPa.

What is the work? What percentage is this of the work of an ideal compressor?



## Real systems: adiabatic reversible

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What is the work? What percentage is this of the work of an ideal compressor?

$$\underline{W = m \cdot [(h_2 - h_1) - (p_2 v_2 - p_1 v_1)]}$$

$$p_1 = 2 \text{ MPa} = 2 \cdot 10^6 \text{ Pa}$$

$$p_2 = 8 \text{ MPa} = 8 \cdot 10^6 \text{ Pa}$$

$$v_1 = 10^{-1} \frac{\text{m}^3}{\text{kg}}$$

$$v_2 = 3,5 \cdot 10^{-2} \frac{\text{m}^3}{\text{kg}}$$

$$h_1 = 2,8 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$

$$h_2 = 3,1 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$

$$W = 1 \text{ kg} \cdot [0,3 \cdot 10^6 \frac{\text{J}}{\text{kg}} - (2,8 \cdot 10^5 \frac{\text{J}}{\text{kg}} - 2 \cdot 10^5 \frac{\text{J}}{\text{kg}})]$$

$$= 2,2 \cdot 10^5 \text{ J} = 220 \text{ kJ}$$

$$W_{id} = m \cdot (h_2 - h_1) = 300 \text{ kJ} \rightarrow \frac{W}{W_{id}} \cdot 100\% = 73\%$$

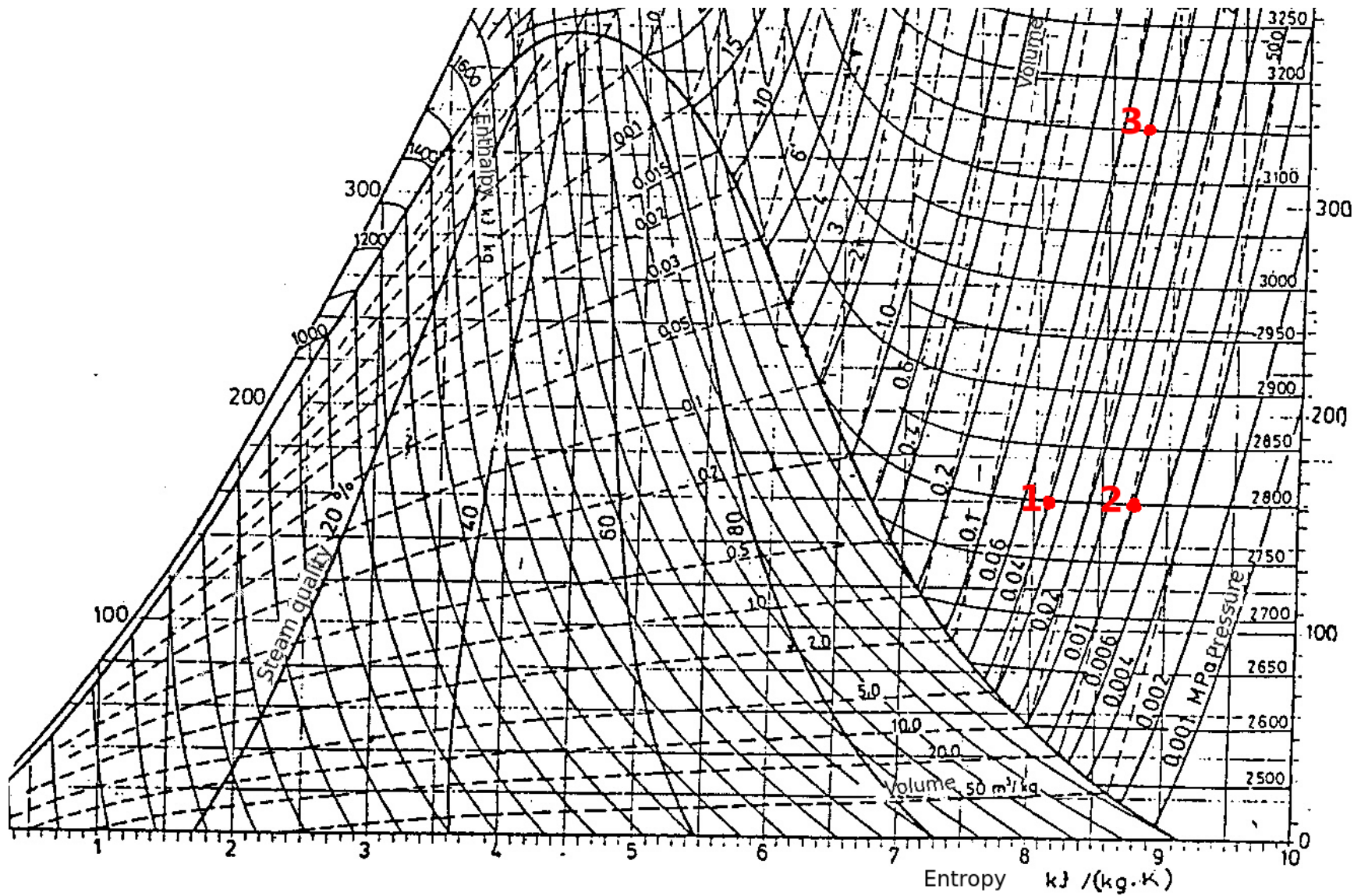
## Real systems: cycle

We have 2 g water vapor with  $T_1 = 160\text{ }^\circ\text{C}$  and  $V_1 = 10\text{ dm}^3$ . We

- Decrease its pressure to 10 kPa in an isothermal process
- Then we compress it in an adiabatic reversible process
- Then we return it into its original state in an isobaric process

$\Delta U$ ,  $\Delta S$ ,  $Q$  ?

# Real systems: cycle



## Real systems: cycle

$$v_1 = \frac{10 \text{ dm}^3}{2 \text{ g}} = 5 \frac{\text{m}^3}{\text{kg}}$$

Isothermal

$$p_1 = 0,04 \text{ MPa} = 4 \cdot 10^4 \text{ Pa} \quad \Delta S_1 = m \cdot (s_2 - s_1) = 1,3 \frac{\text{J}}{\text{K}}$$

$$h_1 = 2,8 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$

$$Q_1 = T_1 \cdot \Delta S_1 = 563 \text{ J} \quad (T_1 \text{ in K !!!})$$

$$s_1 = 8,1 \cdot 10^3 \frac{\text{J}}{\text{kgK}}$$

$$\Delta U_1 = m \cdot [(h_2 - h_1) - (p_2 v_2 - p_1 v_1)] = 0 \text{ J}$$

$$v_2 = 2 \cdot 10 \frac{\text{m}^3}{\text{kg}}$$

Adiabatic reversible

$$p_2 = 0,01 \text{ MPa} = 10^4 \text{ Pa}$$

$$\Delta S_2 = 0 \frac{\text{J}}{\text{K}}$$

$$h_2 = 2,8 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$

$$Q_2 = 0 \text{ J}$$

$$s_2 = 8,75 \cdot 10^3 \frac{\text{J}}{\text{kgK}}$$

$$\Delta U_2 = m \cdot [(h_3 - h_2) - (p_3 v_3 - p_2 v_2)] = 500 \text{ J}$$

$$v_3 = 7,5 \frac{\text{m}^3}{\text{kg}}$$

Isobaric

$$p_3 = 0,04 \text{ MPa} = 4 \cdot 10^4 \text{ Pa}$$

$$\Delta S_3 = -\Delta S_1 = -1,3 \frac{\text{J}}{\text{K}}$$

$$h_3 = 3,15 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$

$$Q_3 = m \cdot (h_1 - h_3) = -700 \text{ J}$$

$$s_3 = 8,75 \cdot 10^3 \frac{\text{J}}{\text{kgK}}$$

$$\Delta U_3 = W_3 + Q_3$$

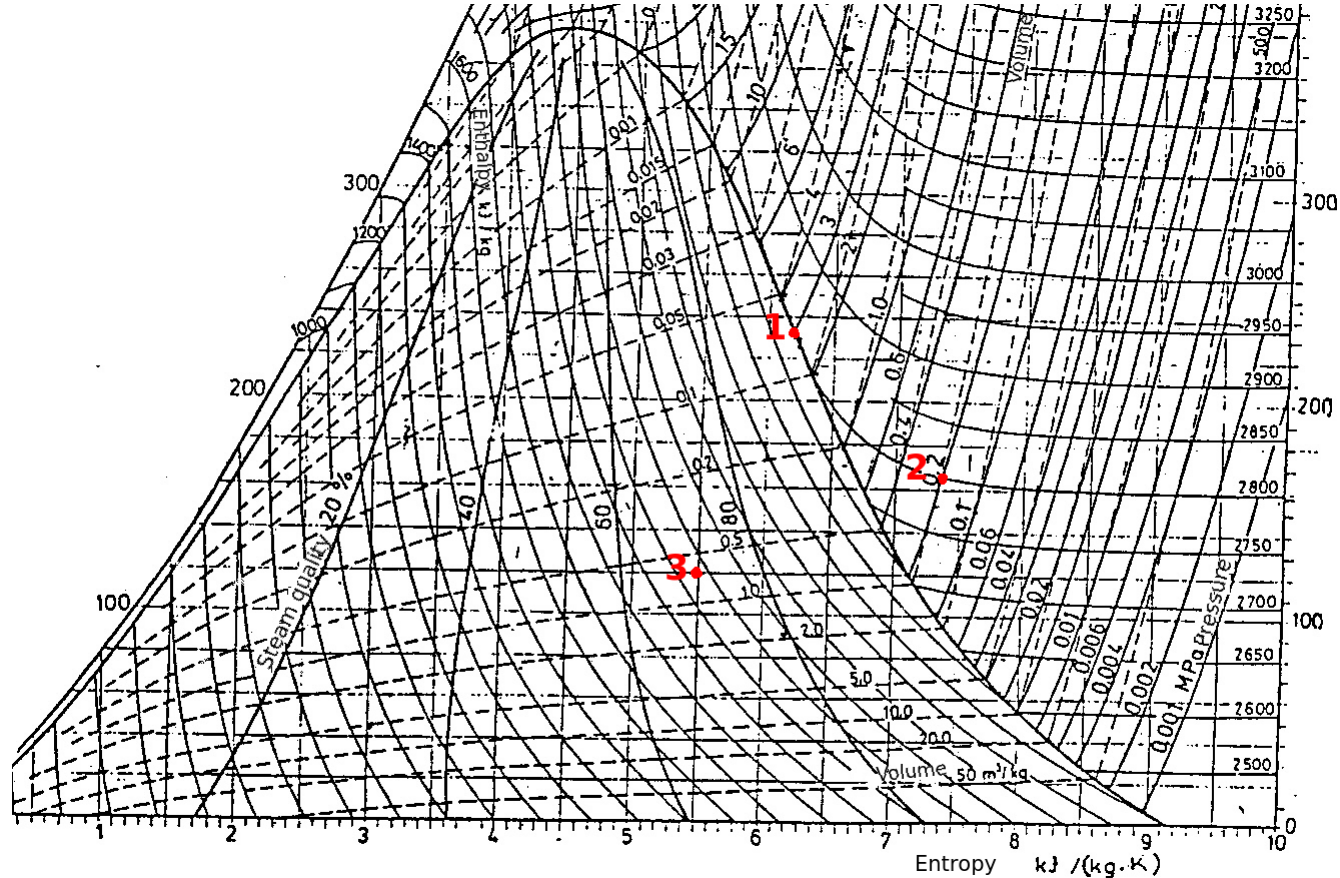
$$= -m \cdot p_3 \cdot (v_1 - v_3) - 700 \text{ J} = -500 \text{ J}$$

# Real systems: heating with steam

We have  $V_1 = 600 \text{ dm}^3$ ,  $p_1 = 3 \text{ MPa}$  saturated vapor. We

- Expand it through an adiabatic throttle to  $200 \text{ kPa}$
- Then we use it for heating in isobaric circumstances, until 30% of the vapor condensates

$Q = ?$





## Real systems: heating with steam

$$Q_1 = 0 \text{ J (adiabatic)}$$

$$Q_2 = \Delta H_2 = m \cdot (h_3 - h_2) \text{ (isobaric)}$$

$$h_3 = 2,05 \cdot 10^6 \text{ J/kg}$$

$$h_2 = h_1 = 2,8 \cdot 10^6 \text{ J/kg}$$

$m = ?$  We have to calculate it from  $V_1$

$$v_1 = 7,5 \cdot 10^{-2} \text{ m}^3/\text{kg} \rightarrow m = V_1/v_1 = \frac{6 \cdot 10^{-1} \text{ m}^3}{7,5 \cdot 10^{-2} \text{ m}^3/\text{kg}} = 8 \text{ kg}$$

$$Q = Q_1 + Q_2 = 8 \text{ kg} \cdot (-0,75 \cdot 10^6 \text{ J/kg}) = -6 \cdot 10^6 \text{ J}$$