Physical Chemistry I. practice

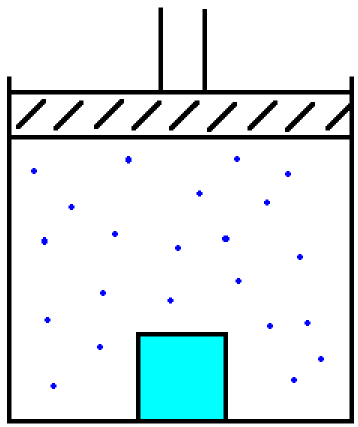
Gyula Samu & Zoltán Rolik

III.: Thermal equilibrium & real gases

rolik@mail.bme.hu

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 enviroment (adiabatic) and at constant pressure (1 bar). What are the equilibrium T and the total ΔS ?



Values of molar heat of vaporization and molar heat of fusion are

$$\lambda_v = 41.4\ kJ/mol$$

$$\lambda_f = 6.02\ kJ/mol$$

The molar heat capacity of the liquid is

$$C_m = 75.312\ J/(mol\ K)$$

and we can suppose that it is temperature independent.

Thermal equilibrium

0th step: What processes will take place?

Melting of ice: $n_{\text{ice}} \cdot \lambda_f = 5\ mol \cdot 6.02\ kJ/mol = \underline{30.1}\ kJ$

Condenstaion of vapor: $n_{\text{vapor}} \cdot \lambda_v = 1\ mol \cdot \underline{-41.4}\ kJ/mol$

$\rightarrow$ There remains some vapor after all of the ice melted

Heating up the water from the ice from 0 °C to 100 °C:

$n_{\text{ice}} \cdot C_m \cdot \Delta T = 5\ mol \cdot 75.312\ J/(mol\ K) \cdot (373\ K - 273\ K) = \underline{37.656}\ kJ$

Condensation of remaining vapor: $(-41.4\ kJ + 30.1\ kJ) = \underline{-11.3}\ kJ$

$\rightarrow$ Not enough to heat the liquid to 100 °C

$\rightarrow$ The condensated vapor will cool further and the melted ice warm further

$\rightarrow$ Equilibrium system is liquid water with $0\ °C < T_{eq} < 100\ °C$

Thermal equilibrium

The system is adiabatically separated: $Q = 0$

$$Q = Q_{\text{ice}} + Q_{\text{vapor}} = 0$$

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

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

$$0 = 5\ mol \cdot 6.02 \cdot 10^3\ J/mol$$

$$+5\ mol \cdot 75.312\ J/(mol\ K) \cdot (T_{eq} - 273\ K)$$

$$-1\ mol \cdot 41.4 \cdot 10^3\ J/mol$$

$$+1\ mol \cdot 75.312\ J/(mol\ K) \cdot (373\ K - T_{eq})$$

$$\rightarrow T_{eq} = 314.7\ K = 41.7\ °C$$

Thermal equilibrium

Change in entropy? $\mathrm{d}S = \frac{\delta Q_{rev}}{T}$

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

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

Melting of ice: $\Delta S_{\text{ice}\rightarrow\text{liq.}} = \frac{5\ mol \cdot 6.02 \cdot 10^3\ J/mol}{273\ K}$

Heating of liquid from the ice:

$$\Delta S_{\text{liq.}0°\text{C}\rightarrow\text{liq.}41.7°\text{C}} = 5\ mol \cdot 75.312\ J/(mol\ K) \cdot ln\frac{314.7\ K}{273\ K}$$

Condensation of vapor: $\Delta S_{\text{vap.}\rightarrow\text{liq.}} = \frac{1\ mol \cdot (-41.4 \cdot 10^3\ J/mol)}{373\ K}$

Cooling of liquid from the vapor:

$$\Delta S_{\text{liq.}100°\text{C}\rightarrow\text{liq.}41.7°\text{C}} = 1\ mol \cdot 75.312\ J/(mol\ K) \cdot ln\frac{314.7\ K}{373\ K}$$

Thermal equilibrium

$$\sum \Delta S = 40 \ J/K$$

What if we have $n_{\text{vapor}} = 0.01 \ mol$ and $n_{\text{ice}} = 5 \ mol$?

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

Condensation of vapor: $0.01 \ mol \cdot (-41.4 \cdot 10^3 \ J/mol) = \underline{-414} \ J$

Cooling of liquid from vapor to 0 °C:

$$0.01 \ mol \cdot 75.312 \ J/(mol \ K) \cdot (273 \ K - 373 \ K) \hat{\approx} \ \underline{-75} \ J$$

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

Equilibrium: 0 °C, ice/liquid system

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

Thermal equilibrium

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

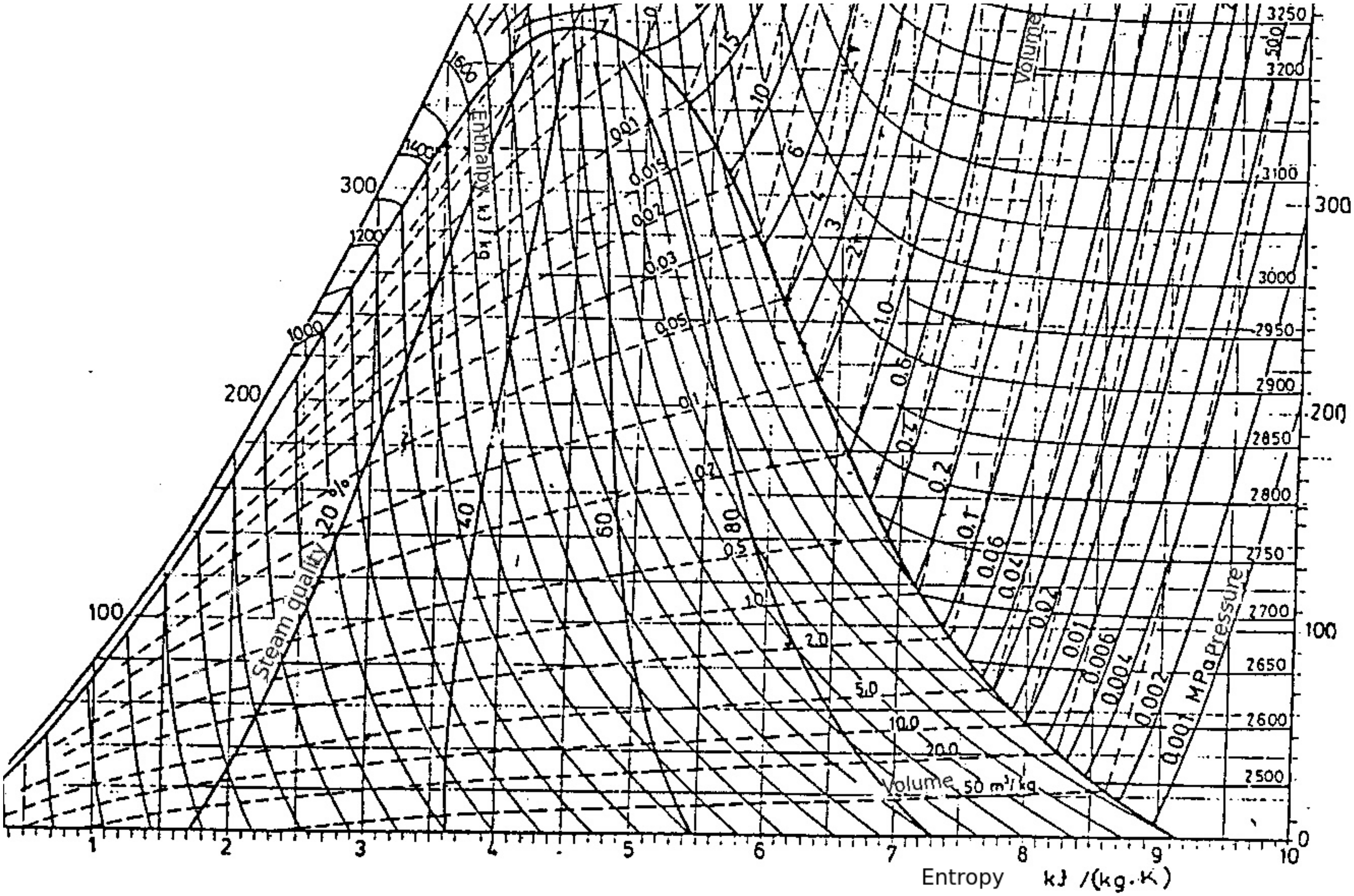
$$\Delta n_{\text{ice}} \cdot \lambda_f - n_{\text{vap.}} \cdot \lambda_v + C_m \cdot n_{\text{vap.}} \cdot \Delta T_{\text{vap.}} = 0\ J$$

$$\rightarrow \Delta n_{\text{ice}} = 0.08\ mol$$

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

$$\rightarrow \Delta S = 0.419\ J/K$$

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: $\Delta V = 0$

$W = 0\ J$
$Q = m \cdot \Delta u = m \cdot (\Delta h - v\Delta p)$

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: $\Delta S = 0$

$Q = 0\ J$
$W = \Delta U$

Adiabatic throttle: $\Delta H = 0$

$Q = 0\ J$
$W = \Delta U = -m \cdot \Delta(pv)$

Ideal compressor: $W = \Delta H$

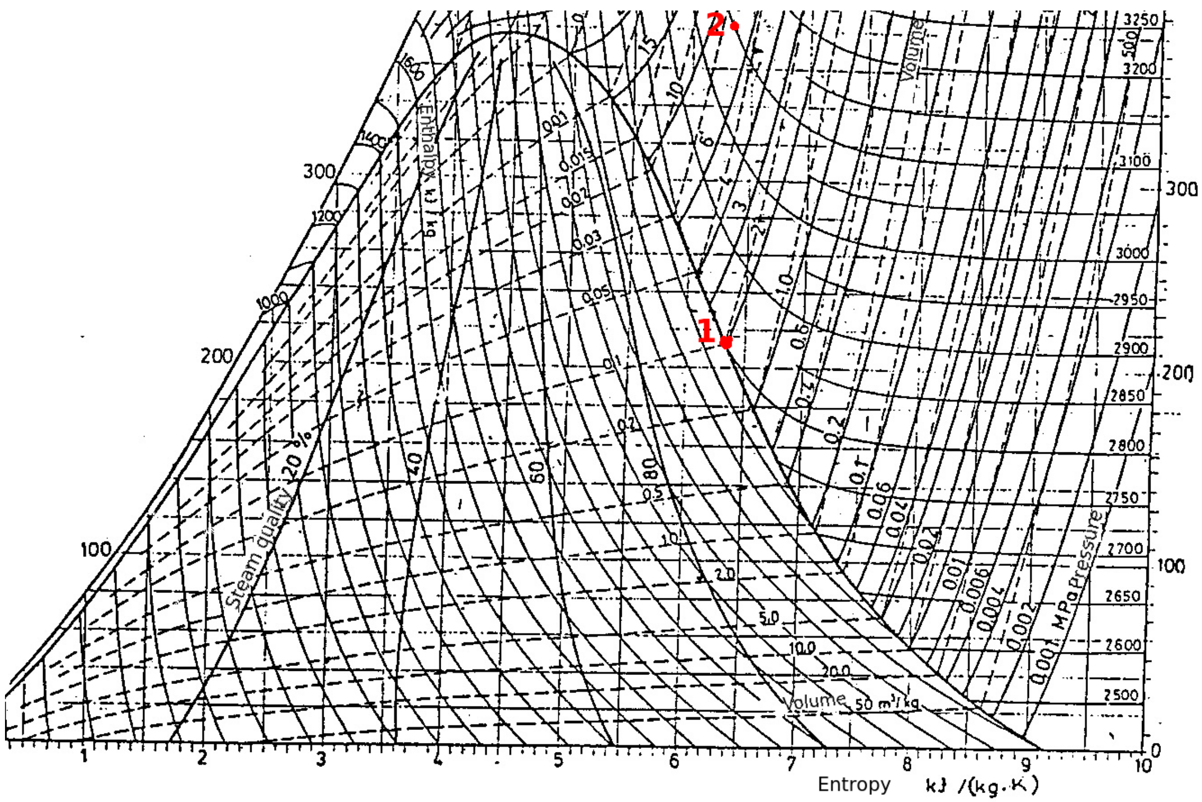
$W = m \cdot \Delta h$
$Q = \Delta U - W = -m \cdot \Delta(pv)$

Real systems: adiabatic reversible

We have 1 $\mathrm{k}g$ saturated water vapor in a cylinder with a piston.

In an adiabatic reversible process we compress it from 2 $\mathrm{M}Pa$ to 8 $\mathrm{M}Pa$.

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



Real systems: adiabatic reversible

We have 1 $\mathrm{k}g$ 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?

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

$$p_1 = 2\ \mathrm{M}Pa = 2 \cdot 10^6\ Pa \qquad p_2 = 8\ \mathrm{M}Pa = 8 \cdot 10^6\ Pa$$

$$v_1 = 10^{-1}\ \frac{m^3}{\mathrm{k}g} \qquad v_2 = 3.5 \cdot 10^{-2}\ \frac{m^3}{\mathrm{k}g}$$

$$h_1 = 2.8 \cdot 10^6\ \frac{J}{\mathrm{k}g} \qquad h_2 = 3.1 \cdot 10^6\ \frac{J}{\mathrm{k}g}$$

$$W = 1\ \mathrm{k}g \cdot [0.3 \cdot 10^6\ \frac{J}{\mathrm{k}g} - (2.8 \cdot 10^5 \frac{J}{\mathrm{k}g} - 2 \cdot 10^5 \frac{J}{\mathrm{k}g})]$$

$$= 2.2 \cdot 10^5\ J = 220\ kJ$$

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

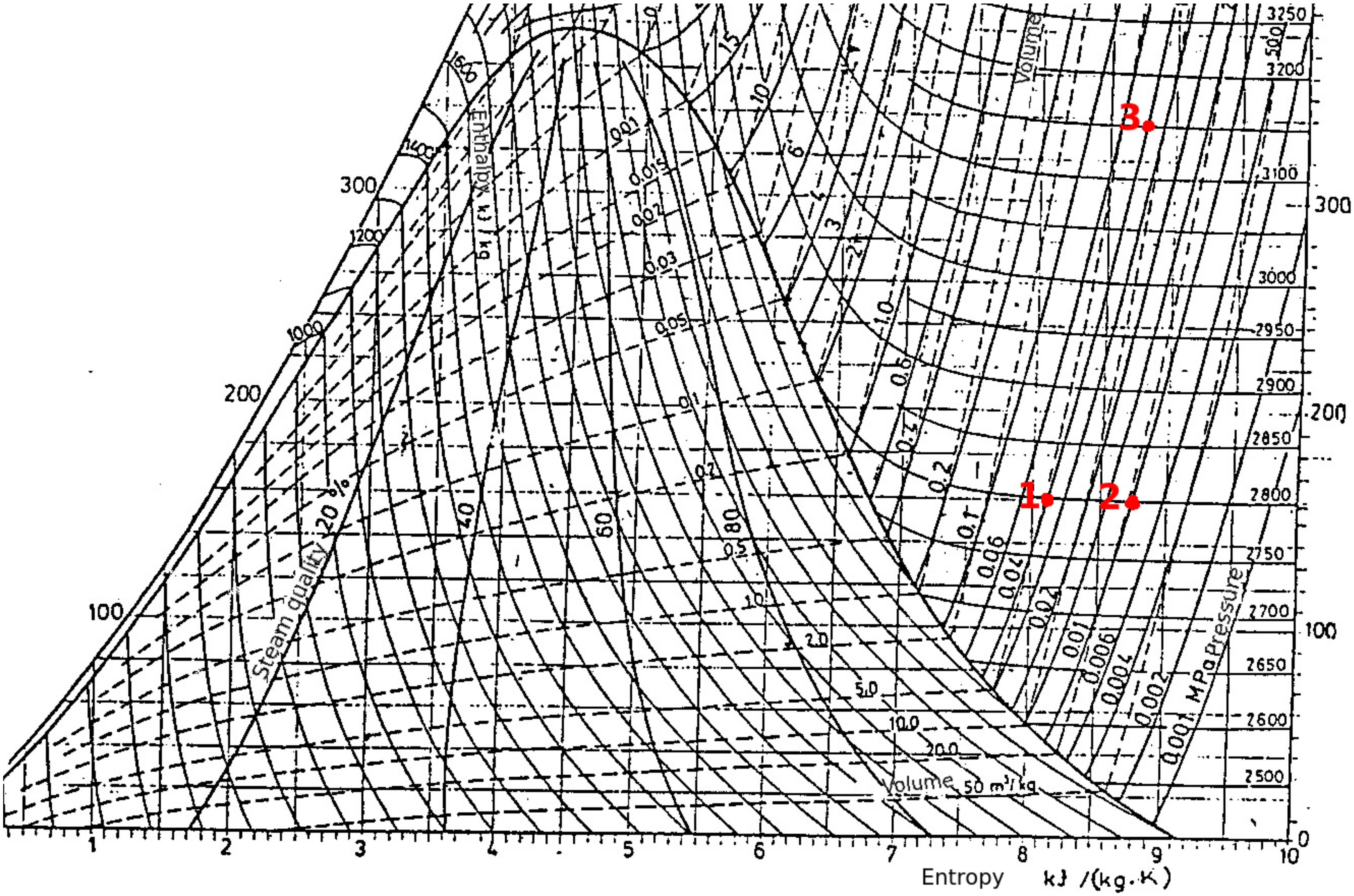
Real systems: cycle

We have 2 g water vapor with $T_1 = 160\ ^{\circ}C$ and $V_1 = 10\ \mathrm{d}m^3$. 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 orignal state in an isobaric process

ΔU, ΔS, Q ?

Real systems: cycle



Real systems: cycle

$v_1 = \frac{10\ \mathrm{d}m^3}{2\ g} = 5\frac{m^3}{\mathrm{kg}}$

$p_1 = 0.04\ \mathrm{M}Pa = 4 \cdot 10^4\ Pa$

$h_1 = 2.8 \cdot 10^6 \frac{J}{\mathrm{kg}}$

$s_1 = 8.1 \cdot 10^3 \frac{J}{\mathrm{kg}K}$

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

$p_2 = 0.01\ \mathrm{M}Pa = 10^4\ Pa$

$h_2 = 2.8 \cdot 10^6 \frac{J}{\mathrm{kg}}$

$s_2 = 8.75 \cdot 10^3 \frac{J}{\mathrm{kg}K}$

$v_3 = 7.5\frac{m^3}{\mathrm{kg}}$

$p_3 = 0.04\ \mathrm{M}Pa = 4 \cdot 10^4\ Pa$

$h_3 = 3.15 \cdot 10^6 \frac{J}{\mathrm{kg}}$

$s_3 = 8.75 \cdot 10^3 \frac{J}{\mathrm{kg}K}$

Isothermal

$\Delta S_1 = m \cdot (s_2 - s_1) = 1.3\ \frac{J}{K}$

$Q_1 = T_1 \cdot \Delta S_1 = 563\ J$ (T_1 in K !!!)

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

Adiabatic reversible

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

$Q_2 = 0\ J$

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

Isobaric

$\Delta S_3 = -\Delta S_1 = -1.3\ \frac{J}{K}$

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

$\Delta U_3 = W_3 + Q_3$

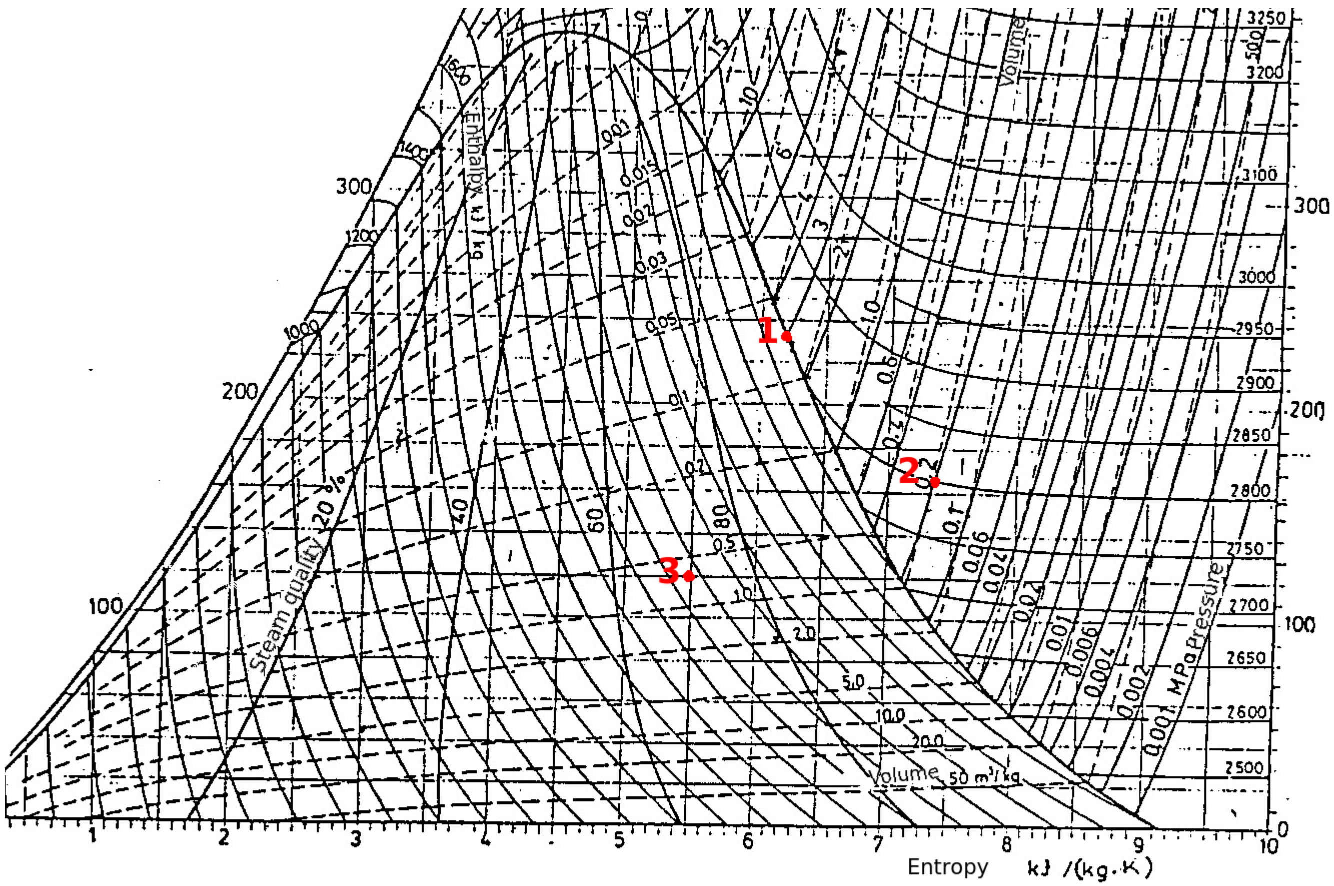
$= -m \cdot p_3 \cdot (v_1 - v_3) - 700\ J = -500\ J$

Real systems: heating with steam

We have $V_1 = 600\ \mathrm{d}m^3$, $p_1 = 3\ \mathrm{M}Pa$ saturated vapor. We

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

$Q = $?



Real systems: heating with steam

$Q_1 = 0\ J$ (adiabatic)

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

$h_3 = 2.05 \cdot 10^6\ J/\text{k}g$

$h_2 = h_1 = 2.8 \cdot 10^6\ J/\text{k}g$

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

$v_1 = 7.5 \cdot 10^{-2}\ m^3/\text{k}g \rightarrow m = V_1/v_1 = \frac{6 \cdot 10^{-1}\ mm^3}{7.5 \cdot 10^{-2} m^3/\text{k}g} = 8\ \text{k}g$

$Q = Q_1 + Q_2 = 8\ \text{k}g \cdot (-0.75 \cdot 10^6\ J/\text{k}g) = -6 \cdot 10^6\ J$