Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije

FKITMCMXIX

VODIK – SKLADIŠTENJE, PRIMJENA

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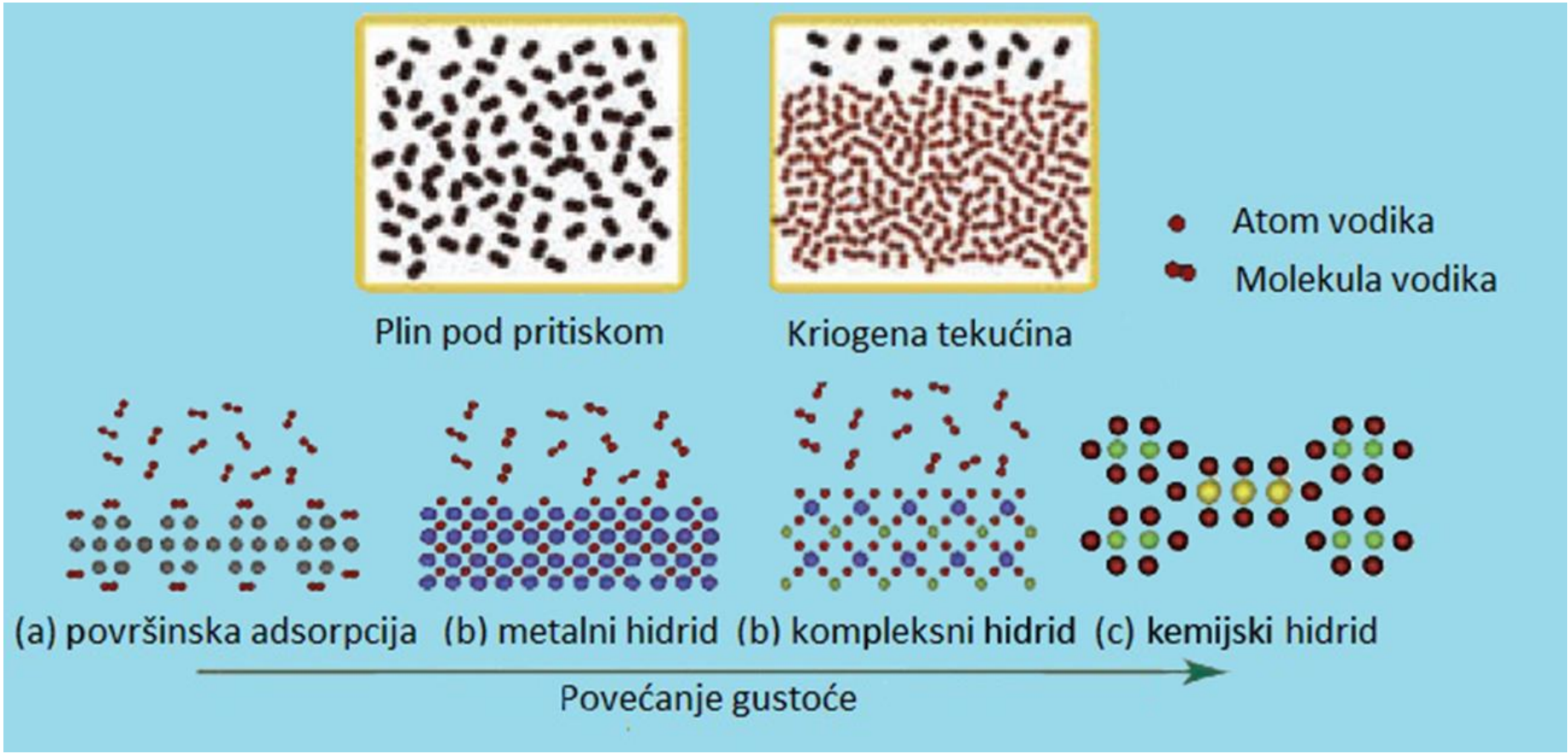
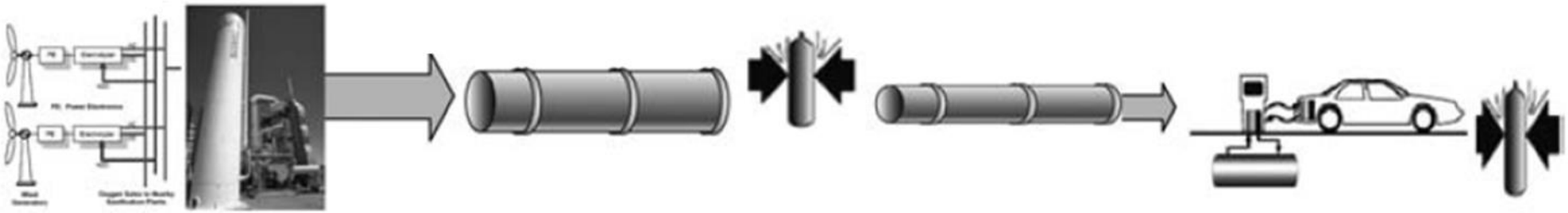
Skladištenje vodika

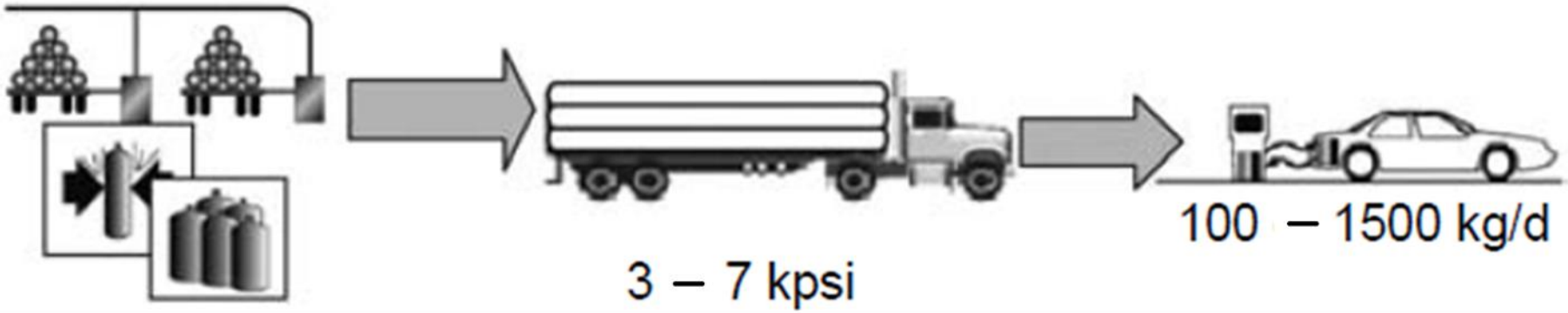
Mogućnosti skladištenja



Plinoviti vodik pod visokim tlakom $H_{2\,(g)}$



100 – 1500 kg/d



3 – 7 kpsi

100 – 1500 kg/d

1 psi ≈ 64895 Pa

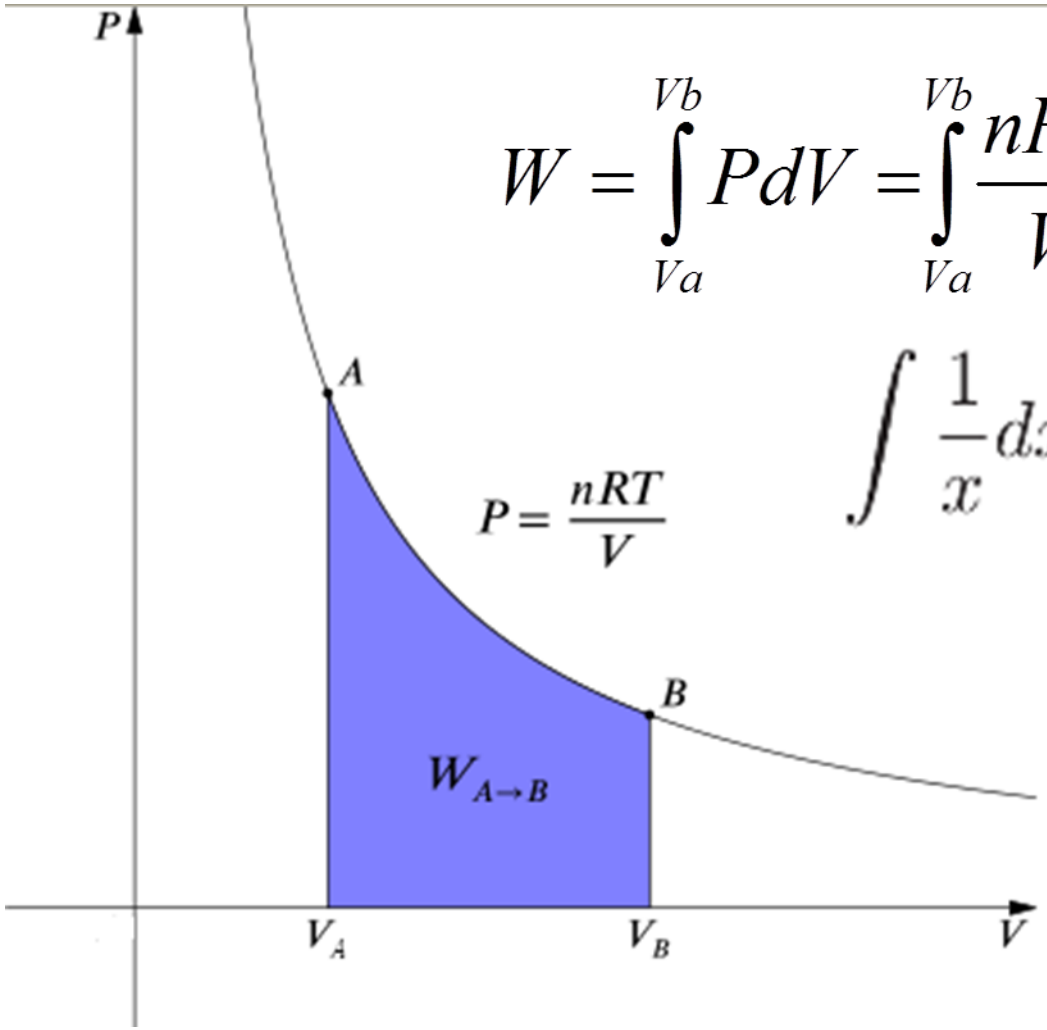
1. ZADATAK

- Kojeg volumena trebaju biti spremnici i koliki rad treba uložiti da bi se 1 kg vodika komprimirao, pri sobnoj temperaturi, pod tlakom od:
- p_1=25 MPa
- p_2=35 MPa
- p_3=70 MPa
- ρ = 0,00008988 g/ml

1. ZADATAK

- $n(\mathrm{H_2}) = \frac{m(\mathrm{H_2})}{M(\mathrm{H_2})} = 496\ \mathrm{mol}$
- $V_{\mathrm{atm}}(\mathrm{H_2}) = n(\mathrm{H_2}) \times V_{\mathrm{m}} = 11117\ \mathrm{L}$
- $V_{\mathrm{atm}}(\mathrm{H_2}) = m(\mathrm{H_2})/\rho(H_2) = 11126\ \mathrm{L}$
- $V_{20\mathrm{bar}}(\mathrm{H_2}) = \frac{p_{\mathrm{atm}}}{p_{20\mathrm{bar}}} \times V_{\mathrm{atm}} = 563{,}67\ \mathrm{L}$
- $V_{25\mathrm{MPa}}(\mathrm{H_2}) = \frac{p_{20bar}}{p_{25\mathrm{MPa}}} \times V_{20\mathrm{bar}} = 45{,}09\ \mathrm{L}$
- $V_{35\mathrm{MPa}}(\mathrm{H_2}) = \frac{p_{20bar}}{p_{35\mathrm{MPa}}} \times V_{20\mathrm{bar}} = 32{,}21\ \mathrm{L}$
- $V_{70\mathrm{MPa}}(\mathrm{H_2}) = \frac{p_{20bar}}{p_{70\mathrm{MPa}}} \times V_{20\mathrm{bar}} = 16{,}10\ \mathrm{L}$

Izotermalna kompresija



$$W = \int_{Va}^{Vb} P dV = \int_{Va}^{Vb} \frac{nRT}{V} dV$$

$$P = \frac{nRT}{V}$$

$$\int \frac{1}{x} dx = \ln x$$

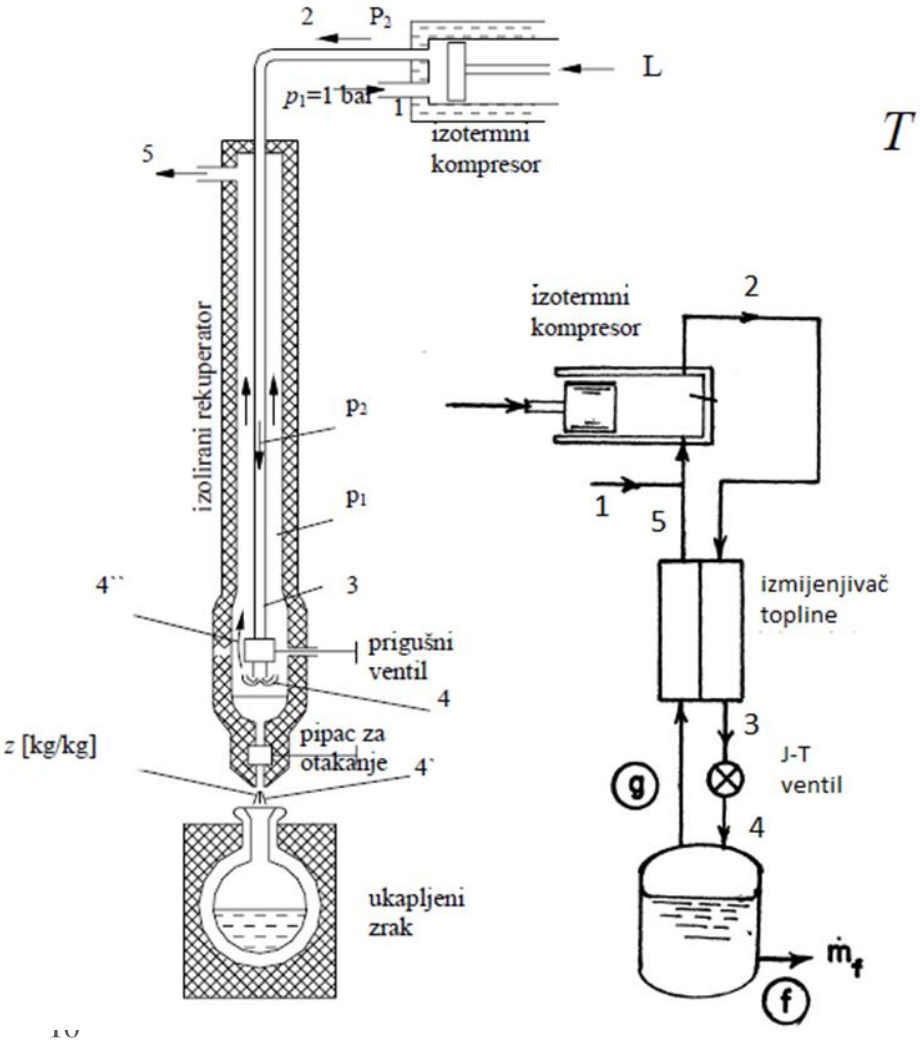
1. ZADATAK

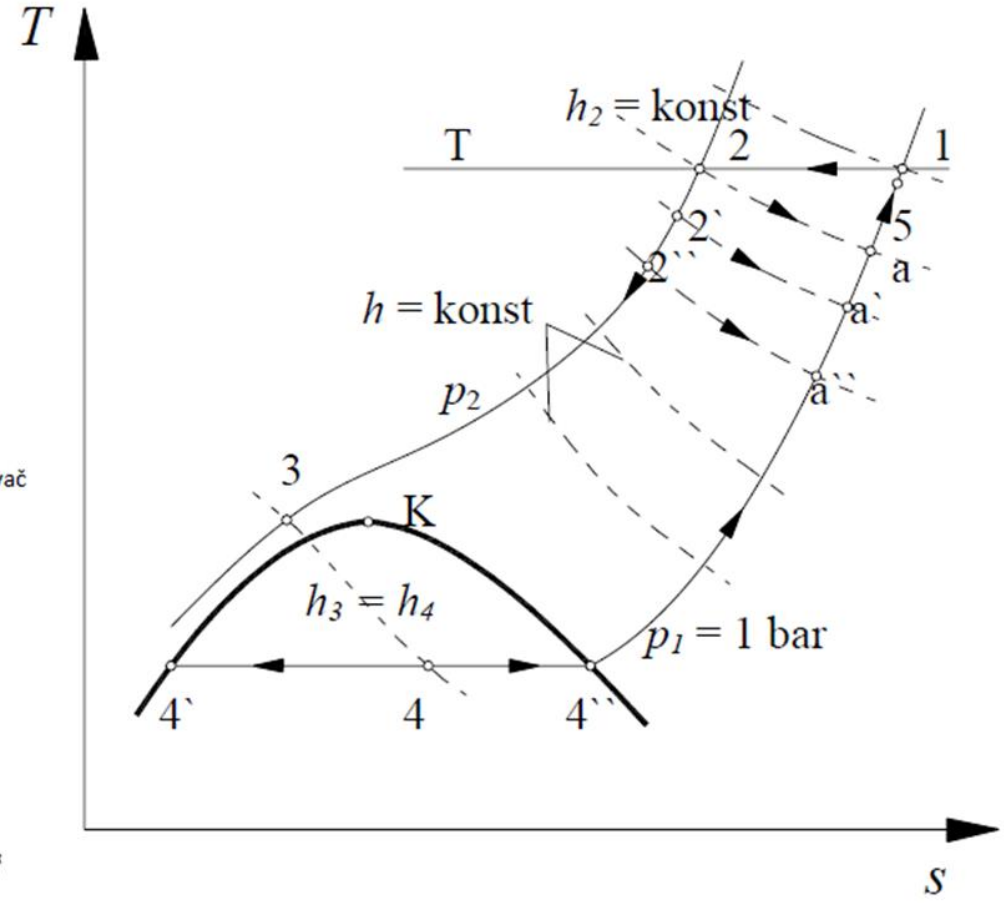
$$W = nRT \ln\left(V_b / V_a\right)$$

- $W_{atm\text{-}\gg 25} = 1{,}880\ \mathrm{kWh}$
- $W_{atm\text{-}\gg 35} = 1{,}995\ \mathrm{kWh}$
- $W_{atm\text{-}\gg 70} = 2{,}232\ \mathrm{kWh}$
- $W_{20bar\text{-}\gg 25} = 0{,}862\ \mathrm{kWh}$
- $W_{20bar\text{-}\gg 35} = 0{,}977\ \mathrm{kWh}$
- $W_{20bar\text{-}\gg 70} = 1{,}214\ \mathrm{kWh}$

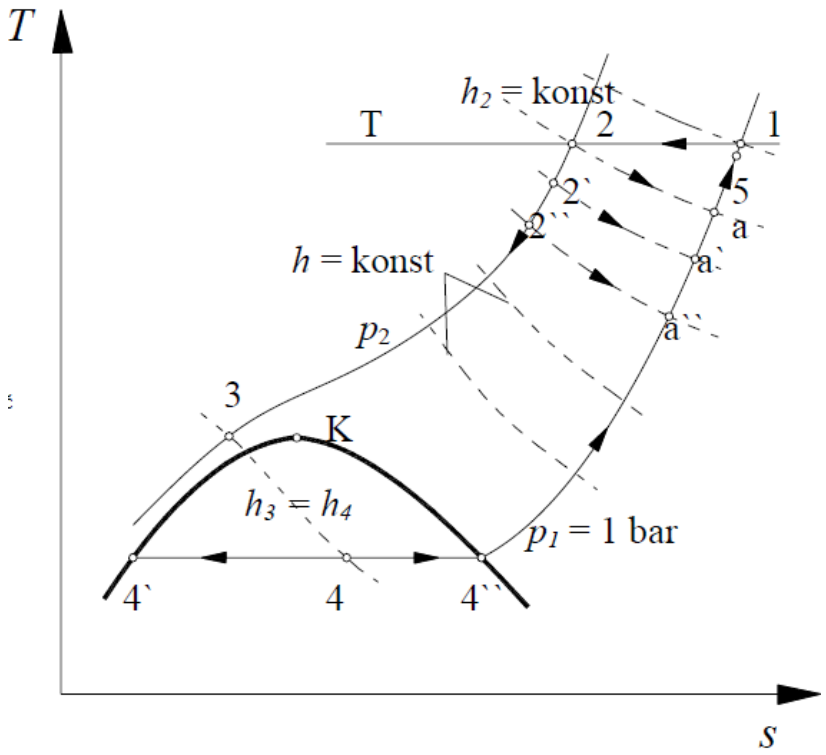
Tekući vodik H_2 (l)

Linde-Hampsonov sustav za ukapljivanje





T, s - dijagram procesa



$$W = T(s_1 - s_2) - (h_1 - h_2)$$

- 1-2 izotermna kompresija p_1 -» p_2
- 2-3 izobarno hlađenje

  T_1 -» T_2
- 3-4 ekspanzija pri konstantnoj entalpiji

  p_2 -» p_1
- 4' vrela kapljevina
- 4" para
- 4-5 izobarno grijanje

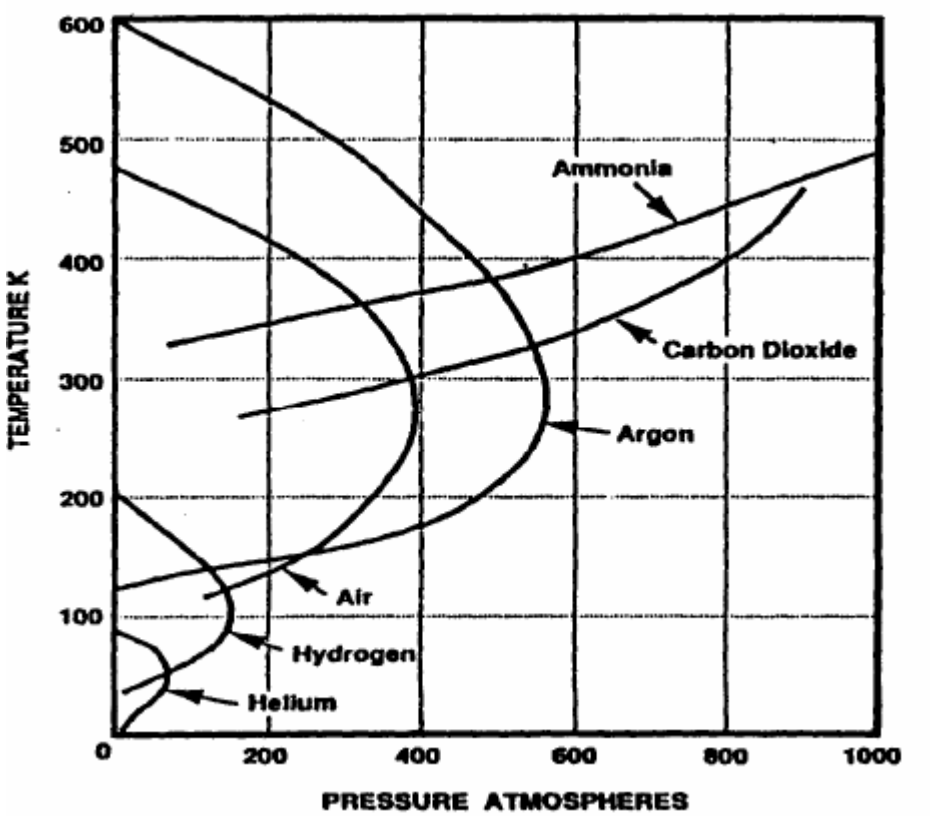
Idealno ukapljivanje vodika

- s_1= 141,29 J/K mol
- h_1= 8515,07 J/mol
- s_2= 36,69 J/K mol
- h_2= 590,15 J/mol
- T = 300 K
- W/kg = 3,232 kWh/kg

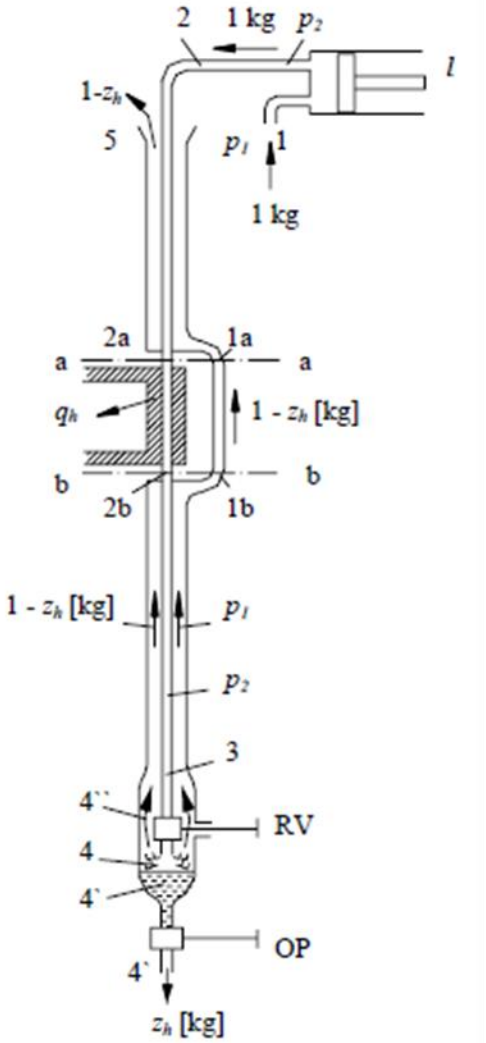
Joule - Thomsonov prigušni učinak

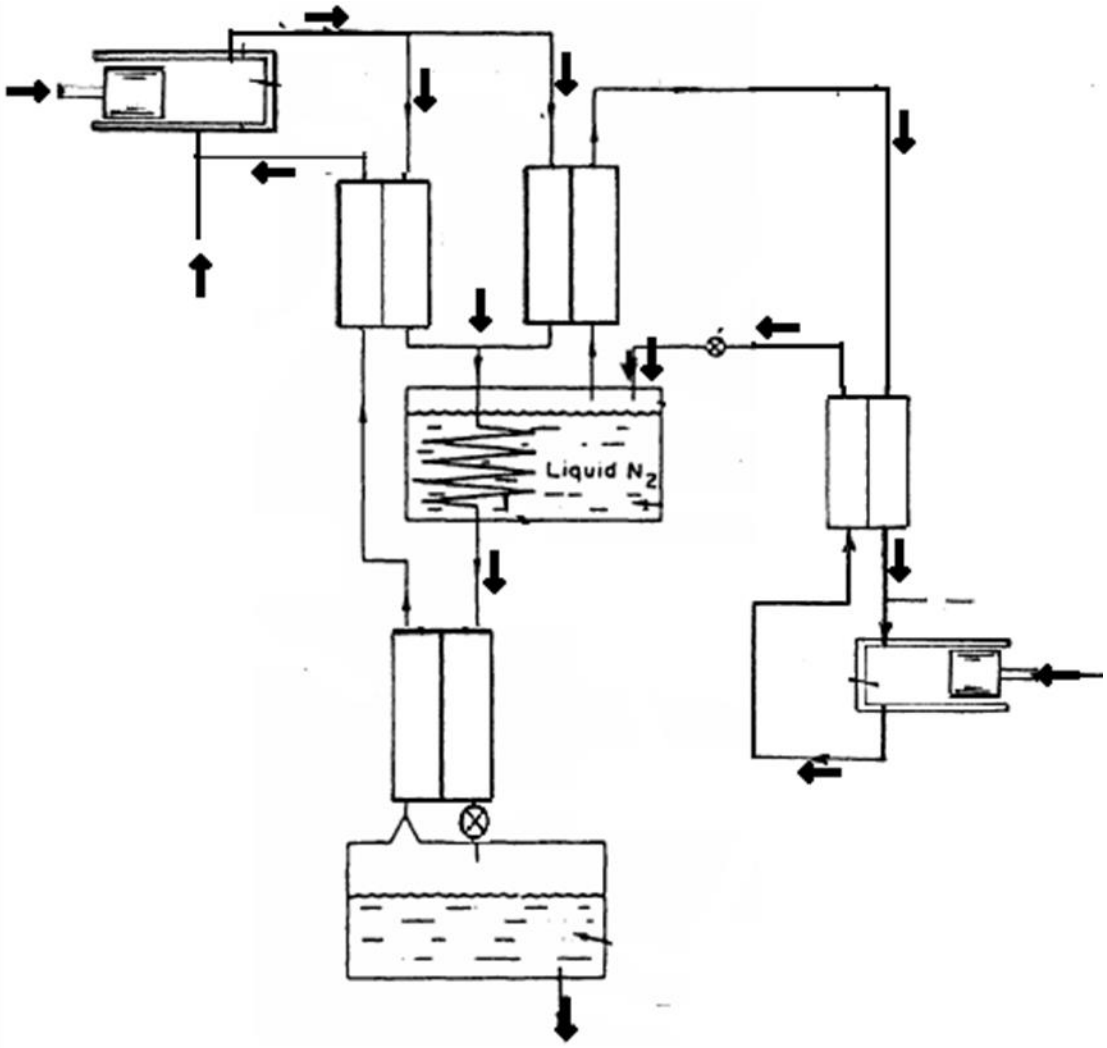
$$\left(\frac{\Delta T}{\Delta p}\right)_h = \frac{T - T_0}{p - p_0}$$

Tvar	T_K	T_{inv0}
Zrak	132,6	≈ 760
H_2	33,18	≈ 200
He	5,19	≈ 40

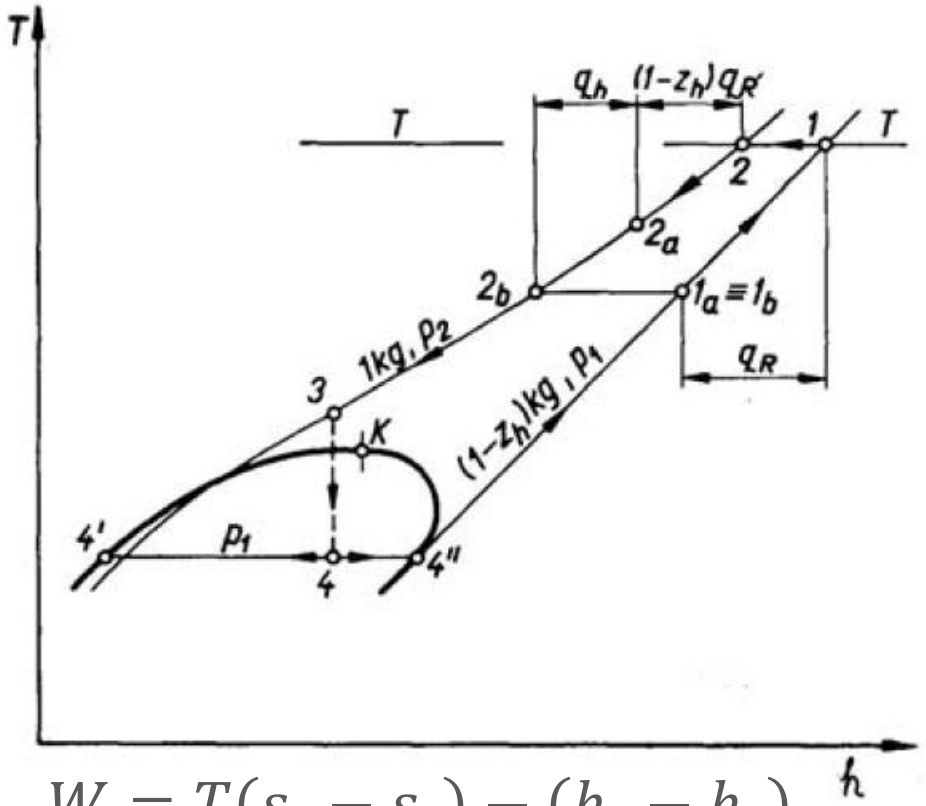


Predhlađenje tekućim dušikom





T, s - dijagram procesa



$$W = T(s_1 - s_2) - (h_1 - h_2) + r\,(T_{N_2}(s_{1N_2} - s_{2N_2}) - (h_{1N_2} - h_{2N_2})$$

- 1-2 izotermna kompresija p_1 -» p_2
- 2-2_a izobarno hlađenje

  T_1 -» T_2
- 2_a–2_b snižavanje temperature pomoću rashladnog sredstva-uređaja T_2 -» T_3
- 2_b-3 izobarno hlađenje

  T_3 -» T_4
- 3-4 ekspanzija pri konstantnoj entalpiji p_2 -» p_1
- 4' vrela kapljevina ; 4'' para
- 4-1 izobarno grijanje

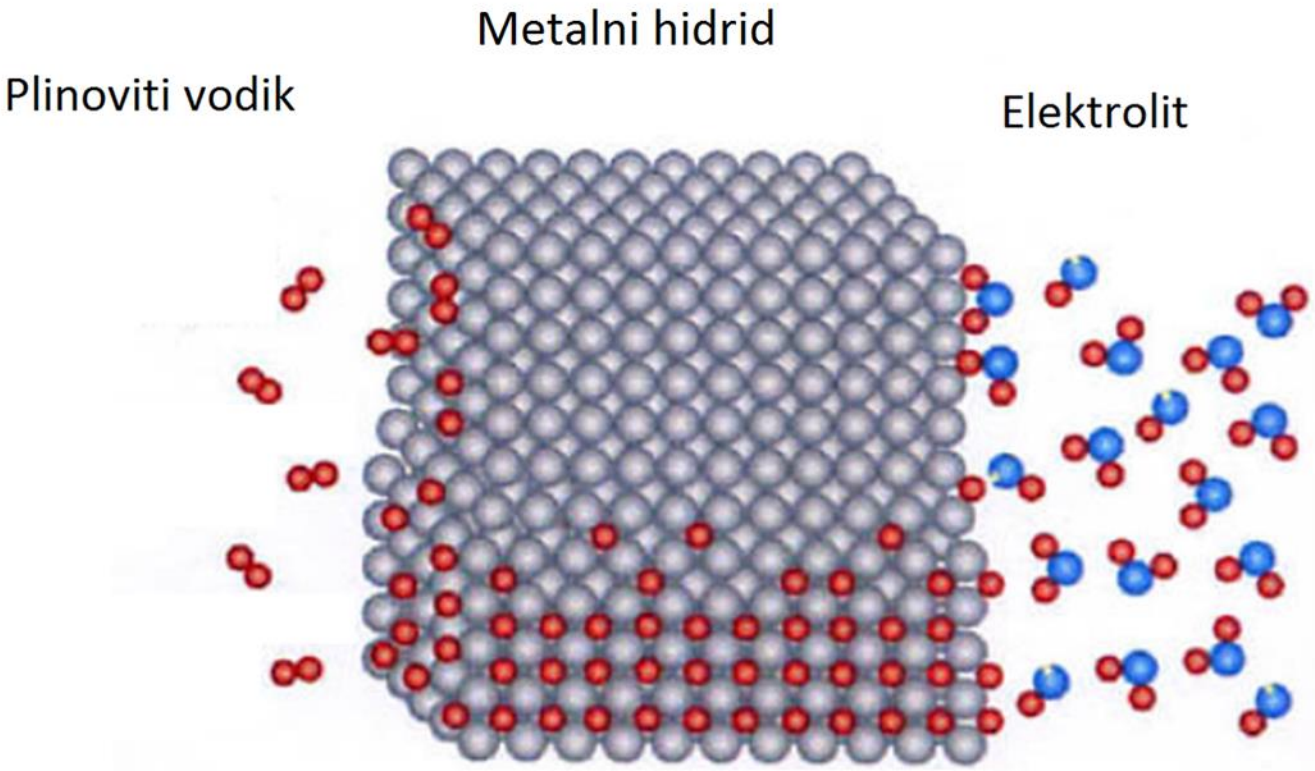
Ukapljivanje dušika

- $s_1 = 4{,}393\ \mathrm{J/K\,g}$
- $h_1 = 460\ \mathrm{J/g}$
- $s_2 = 3{,}033\ \mathrm{J/K\,g}$
- $h_2 = 445\ \mathrm{J/g}$
- $T = 300\ \mathrm{K}$
- $W_{\mathrm{idealno/kg}} = 0{,}109\ \mathrm{kWh}$
- $y = 0{,}09$ y - učinkovitost hlađenja
- $W_{\mathrm{realno/kg}} = 1{,}211\ \mathrm{kWh}$

Ukapljivanje vodika

- $W = T(s_1 - s_2) - (h_1 - h_2) + r\,(T_{N_2}(s_{1N_2} - s_{2N_2}) - (h_{1N_2} - h_{2N_2})$
- s_1= 70,08 J/K g h_1= 4223,75 J/g
- s_2= 32,426 J/K g h_2=4269,72 J/g
- s_{1N_2}= 4,393 J/K g h_{1N_2}= 460 J/g
- s_{2N_2}= 3,033 J/K g h_{2N_2}= 445 J/g
- T_{H_2} =T_{N_2}= 300 K
- r=1; y= 0,081
- $W_{real/kg}$ = 19,778 kWh

Metalni hidridi



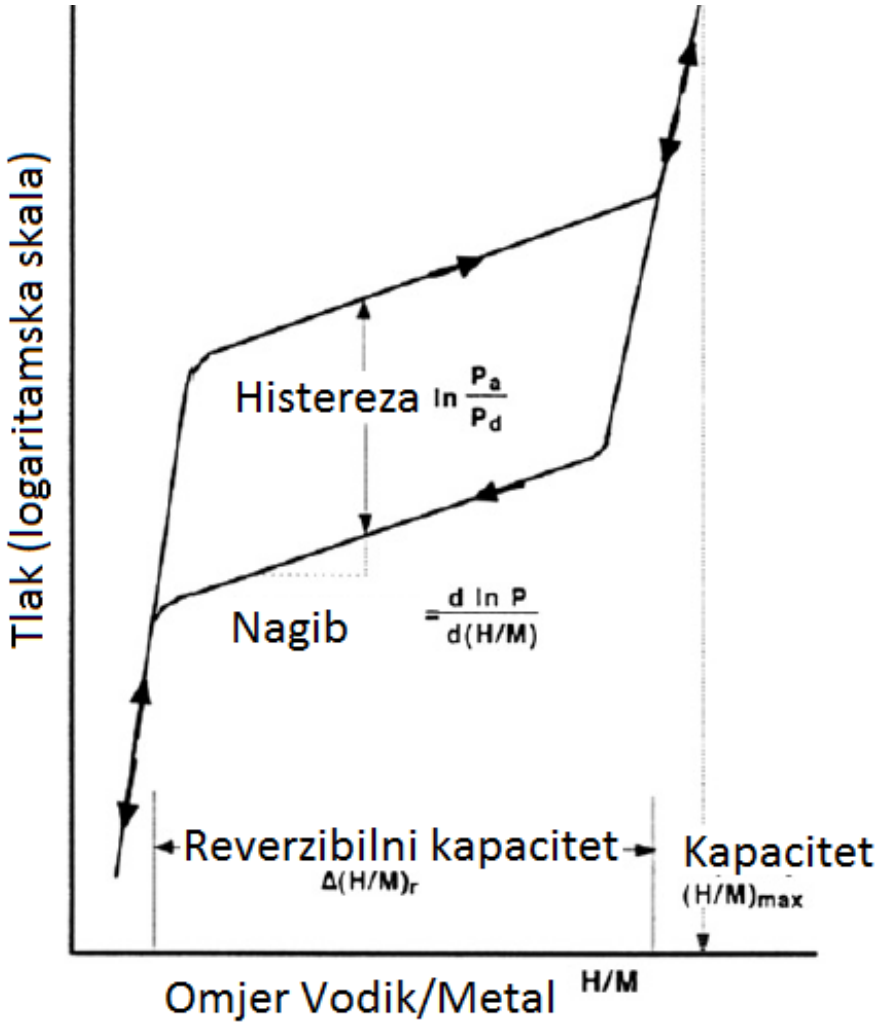
Reakcija iz plinovitog vodika:

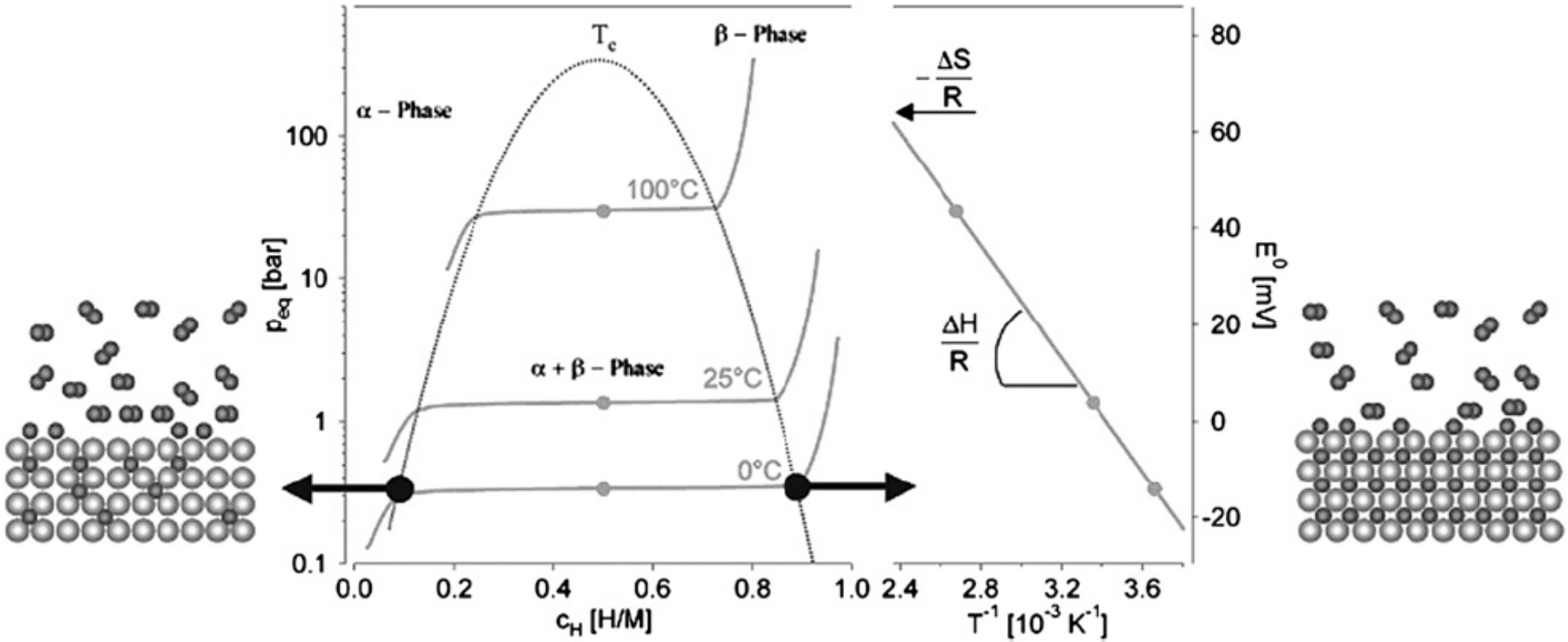
$M + xH_2 \rightarrow MH_y + \text{toplina} \quad (y=2x)$

Elektrokemijska reakcija iz otopine:

$M + xH_2O + xe^- \rightarrow MH_x + xOH^-$

PCT krivulja (pressure-composition-temperature)





Porastom temperature rastu i ravnotežni tlakovi
Odnos između tlaka i temperature zadan je Van't Hoffovom jednadžbom

$$\ln\left(\frac{P_{eq}}{P_{eq}}\right) = \frac{\Delta H}{R}.\frac{1}{T} - \frac{\Delta S}{R}$$

Dok ΔH ovisi o jačini M-H veze i jako varira od metala do metala, ΔS je povezan s tranzicijom molekularnog vodika u atomski vodik (plinovita faza u čvrstu) te je gotovo jednak za sve hidride

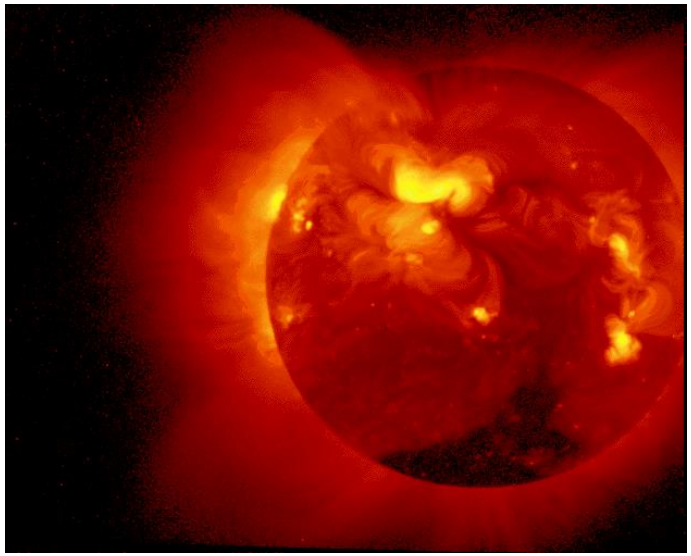
Metalni hidridi

Materijal	Hidrid	Kapacitet (H_2 mas. %)	Pohranjena energija	Entalpija hidrogeniranja
$LaNi_5$	$LaNi_5H_6$	1,3	1,850	30,1
TiFe	$TiFeH_{1,95}$	1,7	2,560	28,1
$ZrMn_2$	$ZrMn_2H_4$	1,7	2,419	53,2
Mg_2Ni	Mg_2NiH_4	7,0	10,000	64,5
Mg	MgH_2	7,7	11,000	74,2

$W_{LaNi5} = 4,147$ kWh

$W_{Mg} = 10,22$ kWh

Primjena vodika



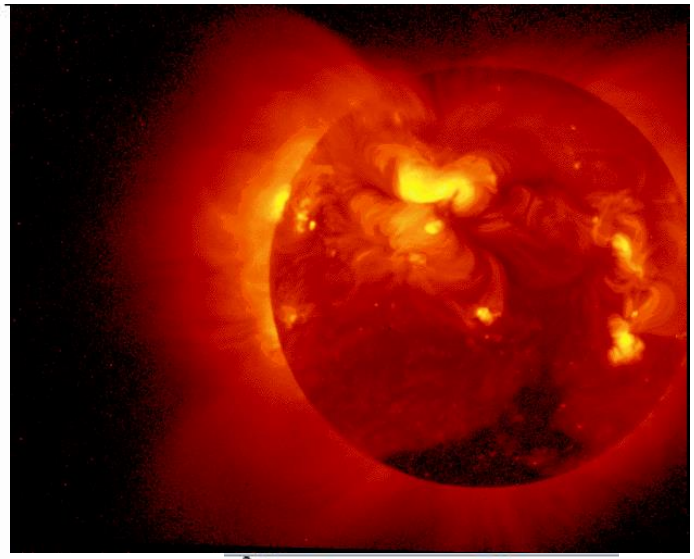
Mogućnosti primjene vodika

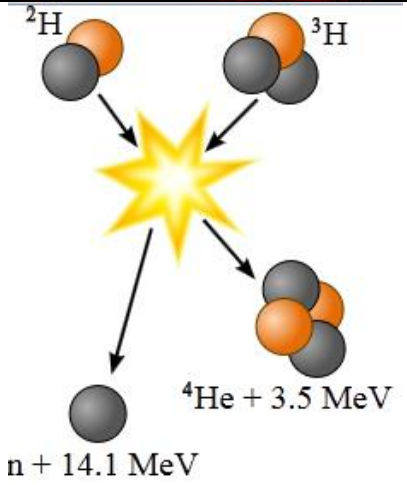
$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$

$H_2\,(g) + O_2\,(g)$

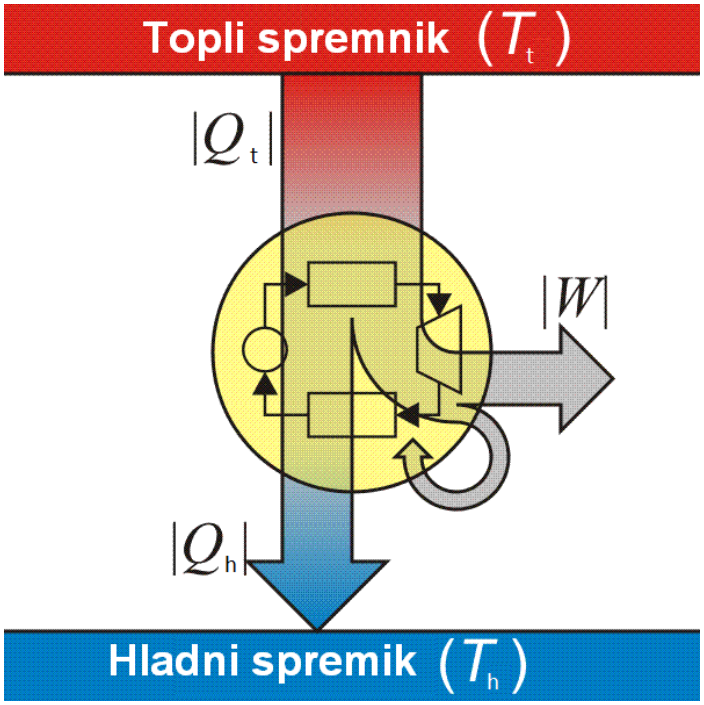
$\downarrow$

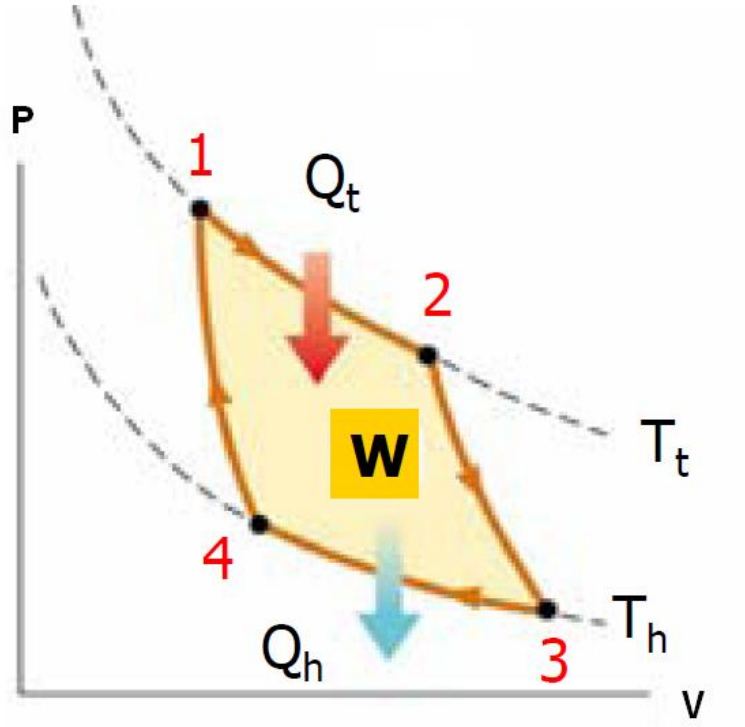
električna struja, E_{MS} + H_2O + toplina





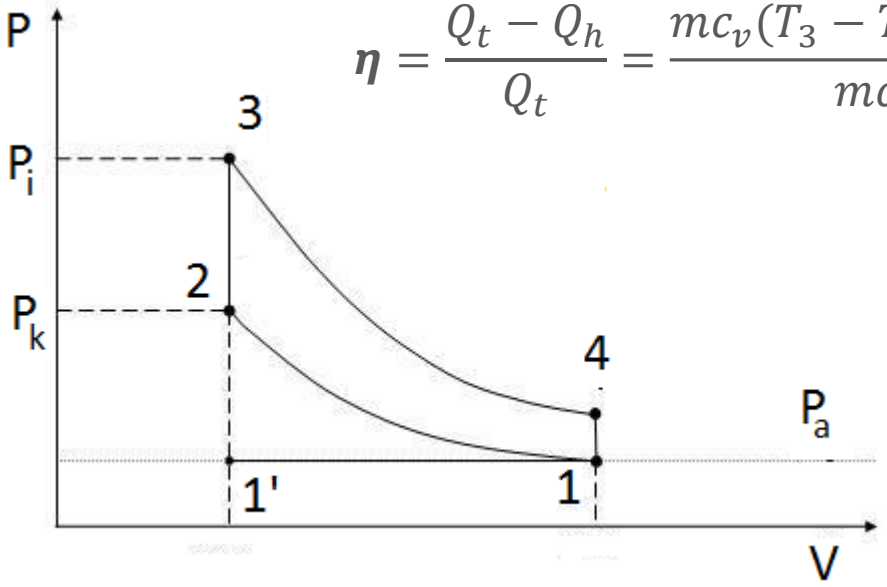
Toplinski motor – Carnotov ciklus



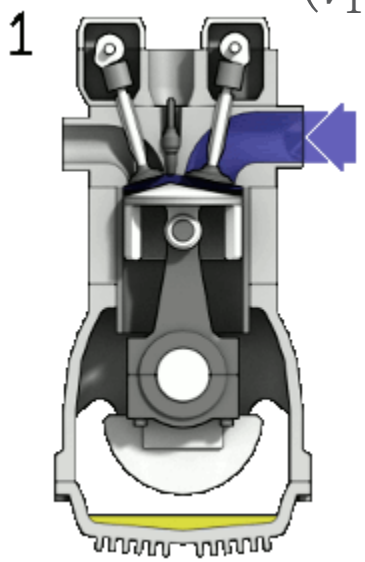


- 1-2 izotermna ekspanzija
- 2-3 adijabatska ekspanzija
- 3-4 izotermna kompresija
- 4-1 adijabatska kompresija

Motor s unutarnjim izgaranjem



$$\eta = \frac{Q_t - Q_h}{Q_t} = \frac{mc_v(T_3 - T_2) - mc_v(T_4 - T_1)}{mc_v(T_3 - T_2)} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\frac{Cp}{Cv}-1}}$$



- Četverotaktni Otto motor
  - 1. takt 1'-1, usis zraka i plinovitog goriva
  - 2. takt 1-2, kompresija i zapaljenje u točci 2
  - 3. takt 2-4, 2-3 izgaranje goriva; 3-4 ekspanzija
  - 4. takt 4-1', 4-1 pad tlaka na atmosferski; 1-1' ispuh plinova van iz komore

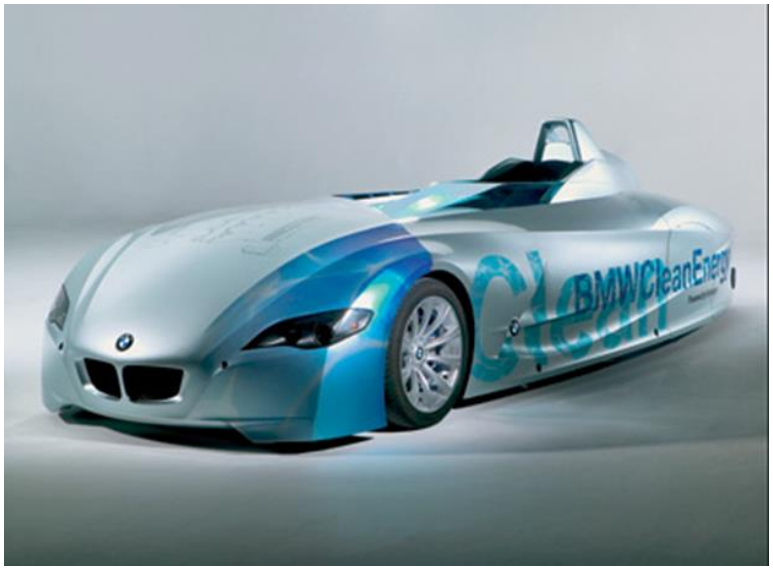
2. ZADATAK

- Koliko je iskorištenje Ottovog motora u slučaju da koristimo:
  - Benzin
  - Vodik

  kao gorivo uz pretpostavku da oba sagorijevaju u istom motoru.

a) $\frac{V_2}{V_1} = 10:1$

b) $\frac{V_2}{V_1} = 17:1$

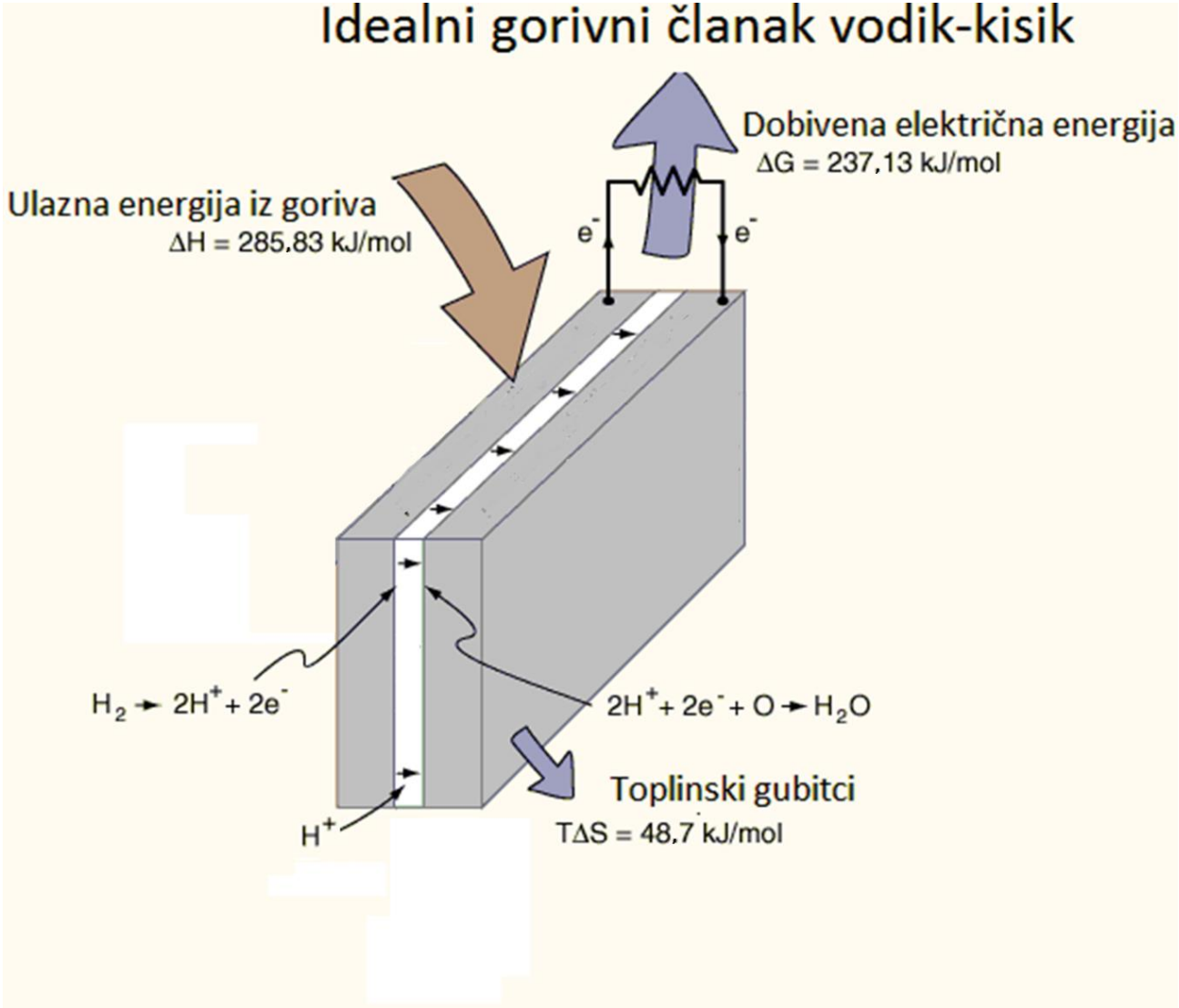


http://www.bmwblog.com/2015/06/11/bmw-considers-hydrogen-fueled-race-car-for-lemans

2. ZADATAK

- $C_p\,(H_2)$=14,32 kJ/kg K $C_v\,(H_2)$= 10,16 kJ/kg K
- C_p (benzin)/C_v(benzin)=1,1
- $\boldsymbol{\eta}(H_2) = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\frac{Cp}{Cv}-1}}$ =0,61
- $\boldsymbol{\eta}(H_2) = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\frac{Cp}{Cv}-1}} = 0{,}69$
- $\boldsymbol{\eta}(\text{benzin}) = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\frac{Cp}{Cv}-1}} = 0{,}21$
- $\boldsymbol{\eta}(\text{benzin}) = 1 - \frac{1}{\left(\frac{V_2}{V_1}\right)^{\frac{Cp}{Cv}-1}} = 0{,}25$

Gorivni članak



Idealna učinkovitost / idelani standardni potencijal

- A(-): $H_2 \rightarrow 2H^+ + 2e^-$
- K(+): $2H^+ + 2e^- \; 1/2O_2 \rightarrow H_2O$
- $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$
- $\Delta H = \left(H_{H_2O} \right) - \left(H_{H_2} + \frac{1}{2} H_{O_2} \right) = -285{,}83 \text{ kJ/mol}$
- $\Delta S = \left(S_{H_2O} \right) - \left(S_{H_2} + \frac{1}{2} S_{O_2} \right) = -163{,}6 \text{ J/K mol}$
- $\Delta G = \Delta H - T\Delta S = -237{,}06 \text{ kJ/mol}$
- $\boldsymbol{\eta}_{ideal} = \frac{\Delta G}{\Delta H} = 0{,}83$
- $E^0 = \frac{\Delta G}{-z \times F} = 1{,}229\text{V}$ Idealni standardni potencijal

Realna učinkovitost gorivnog članka

- $\eta_{\text{realan}} = \frac{E_{\text{članka}} \times I \times \eta_{\text{ideal}}}{E^0 \times I} = \frac{E_{\text{članka}} \times 0{,}83}{1{,}229} = 0{,}675 \times E_{\text{članka}}$