HYDROGEN THE FUTURE ENERGY CARRIER?

ANDREAS ZÜTTEL

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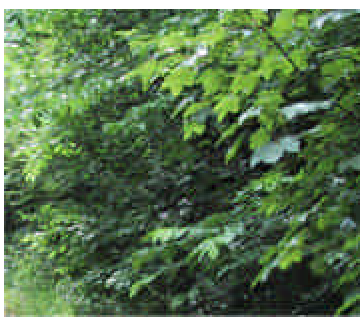
HISTORICAL ENERGY RESOURCES

3000 B.C.

Human power

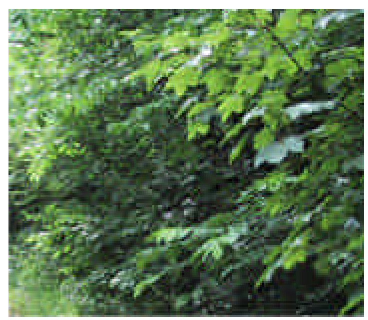


Food, Heat

-CHOH-

1000 B.C.

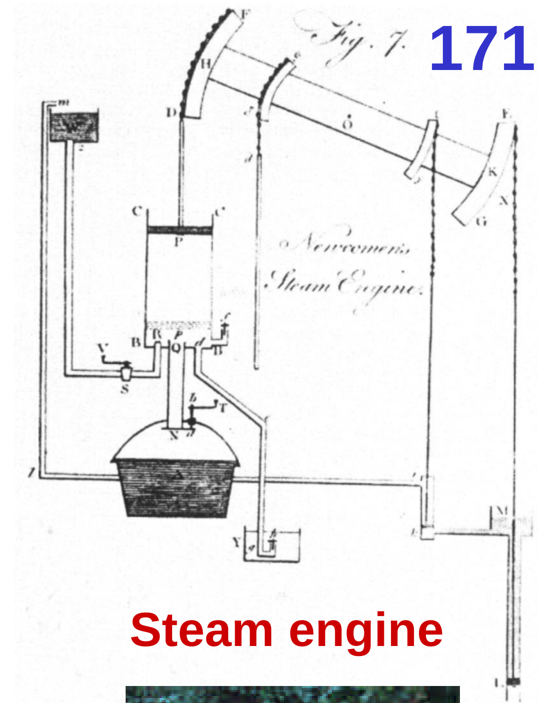
Horse power



Food, Heat

-CHOH-

1712



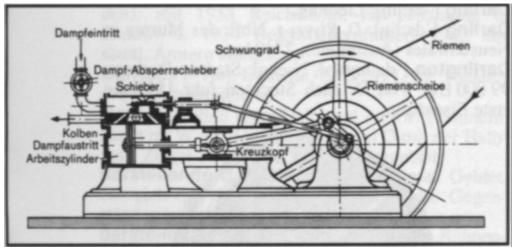
Steam engine

Heat, Work

-CHOH-

HISTORICAL ENERGY RESOURCES

18th century



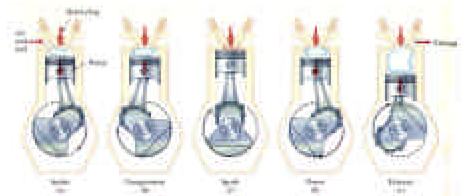
Steam engine

Coal

Heat, Work

C

19th century



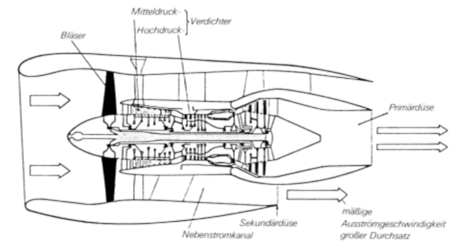
Internal combustion engine

Crude Oil

Heat, Work

$-CH_2-$

20th century



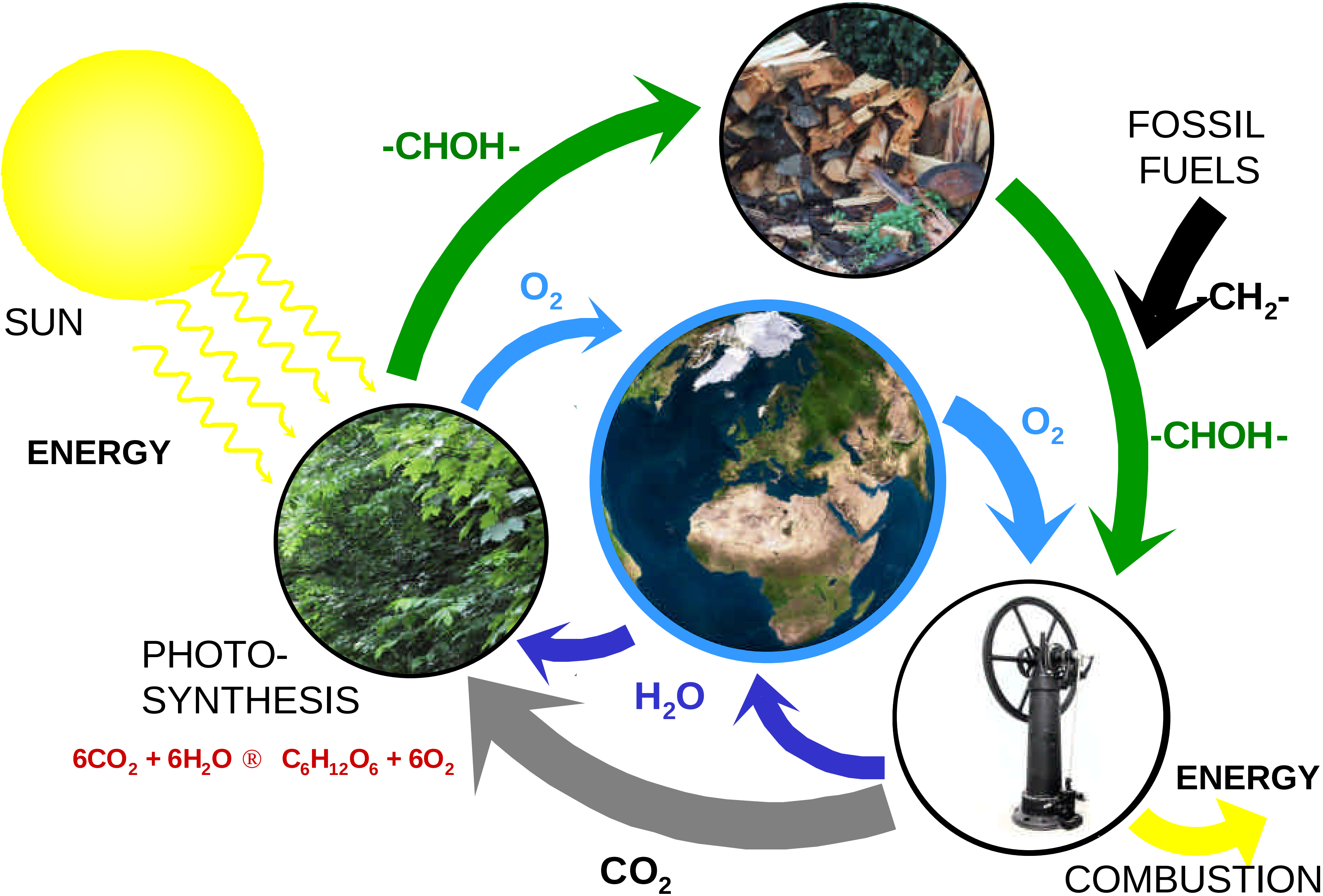
Gasturbine

Natural gas

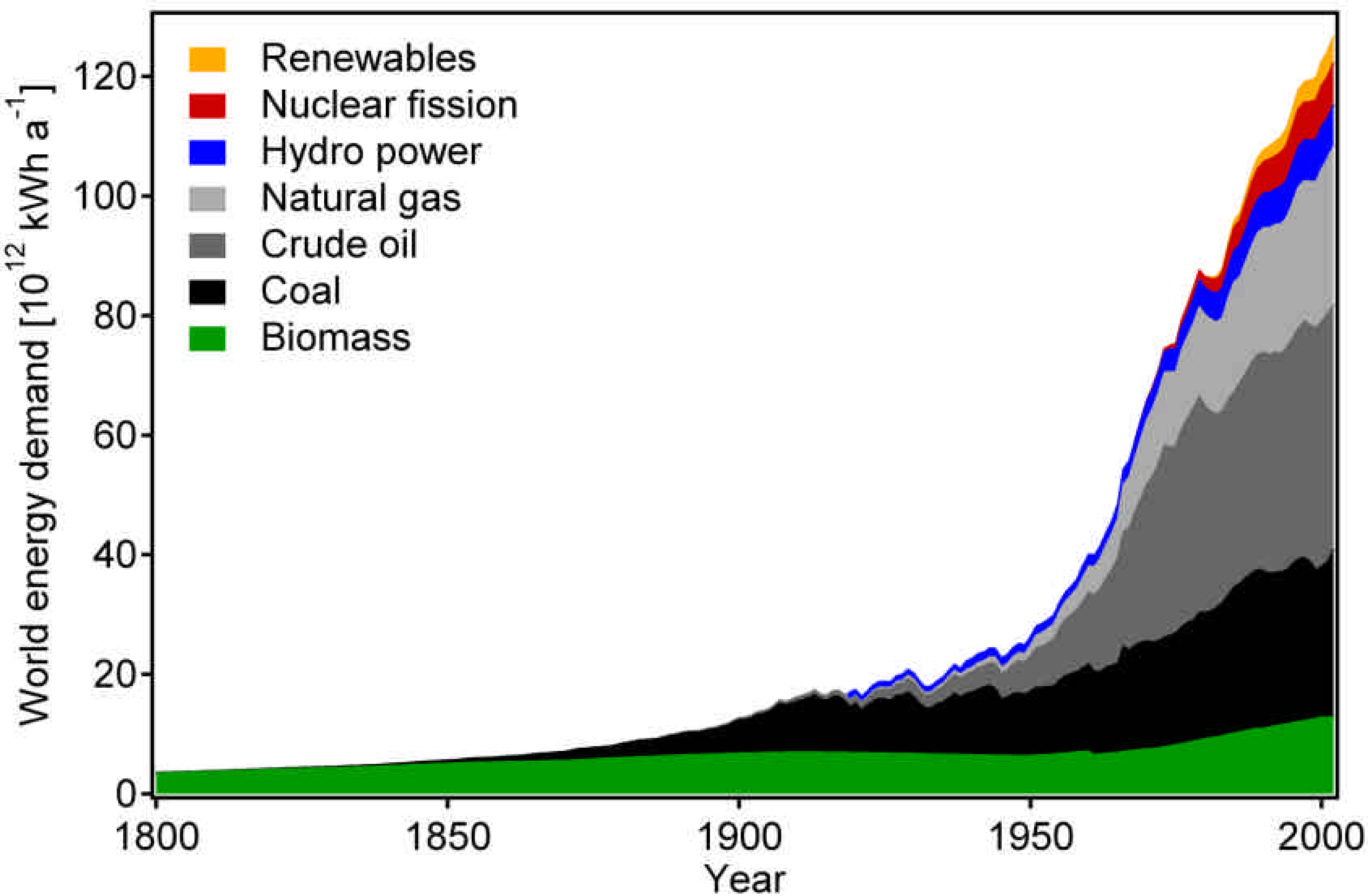
Heat, Work

CH_4

CARBON CYCLE



WORLD ENERGY CONSUMPTION

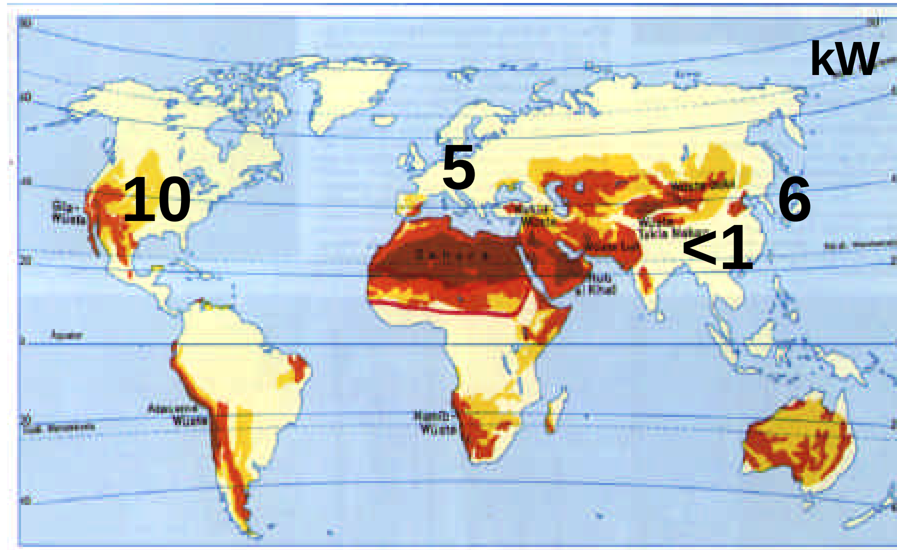


Ref.: Jean-Marie Martin-Amouroux, IEPE, Grenoble, France

ENERGY CONSUMPTION

Energy carrier	Demand	Reserve [years]
Fossile		
Crude Oil	32.7 %	41
Natural Gas	19.5 %	63
Coal	21.4 %	218
Renewable		
Hydropower	6.7 %	
Biomass	11.6 %	
Others	2.0 %	
Nuclear	6.1 %	100

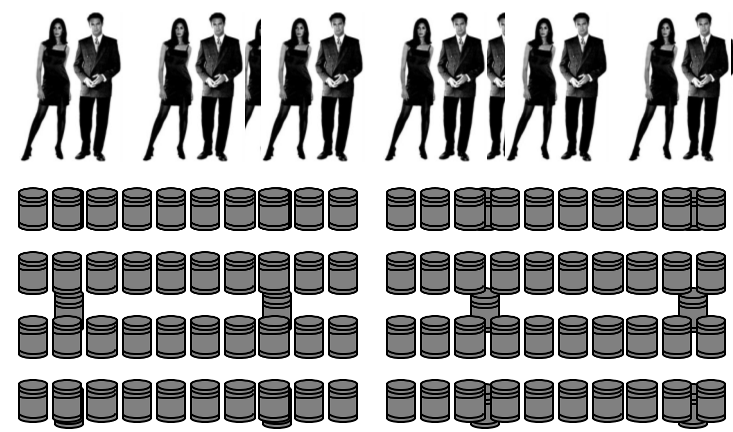
Average Power Consumption per Person



World = **2 kW/person**   for 2 Bil. = **0 kW**

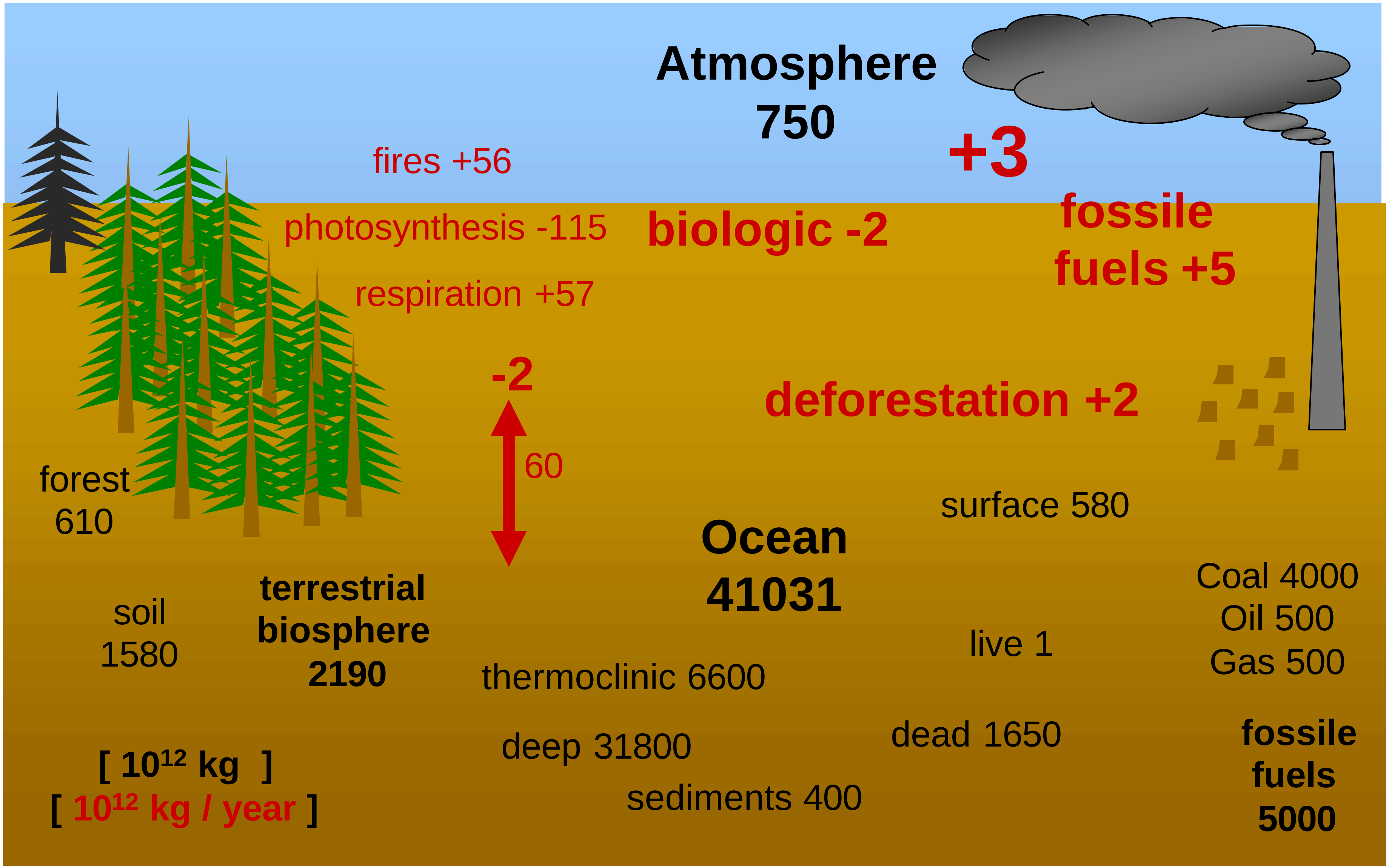
industrialized countries

20th Century



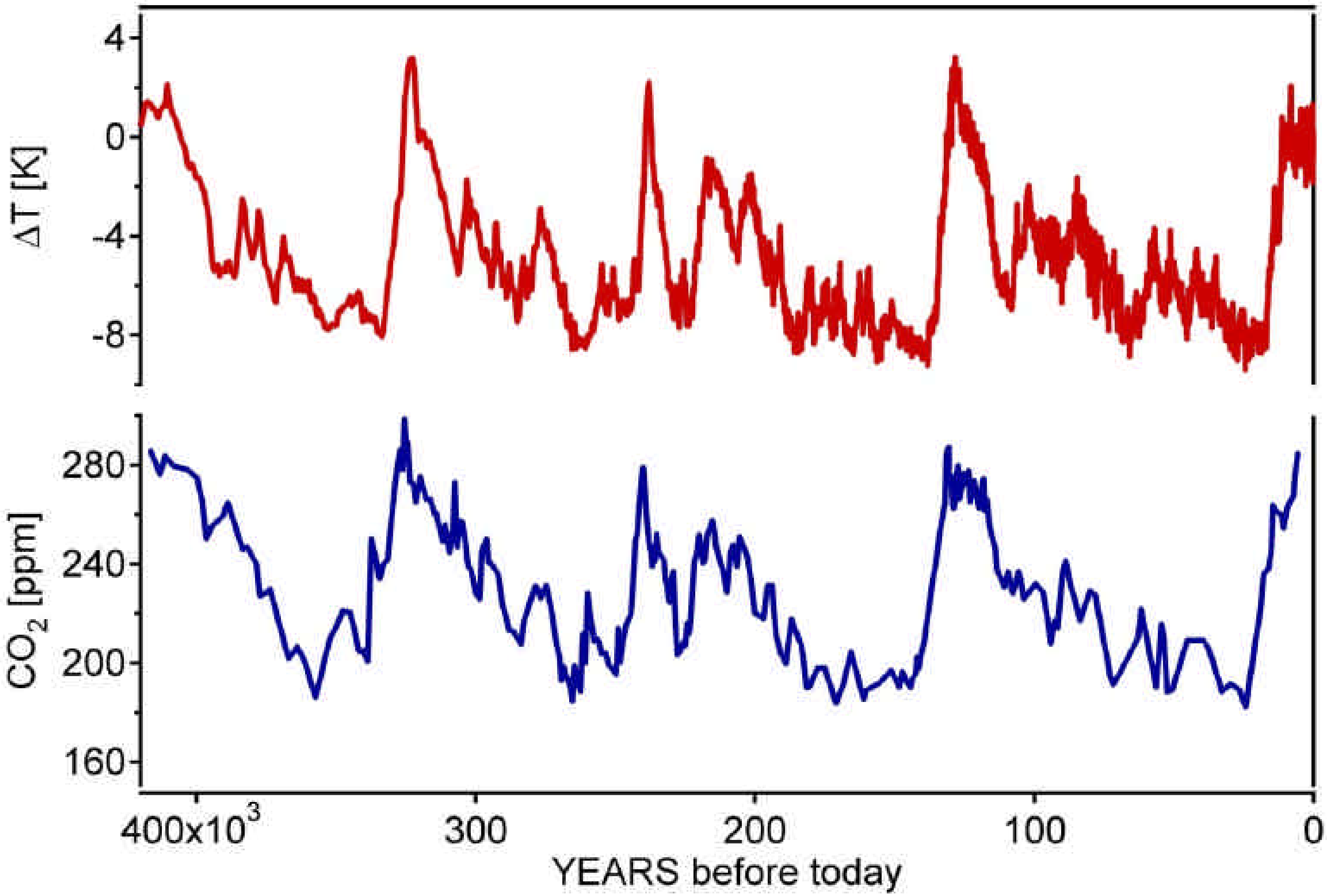
POLUTION DUE TO THE COMBUSTION OF FOSSIL FUELS

WORLD CARBON RESERVOIRS



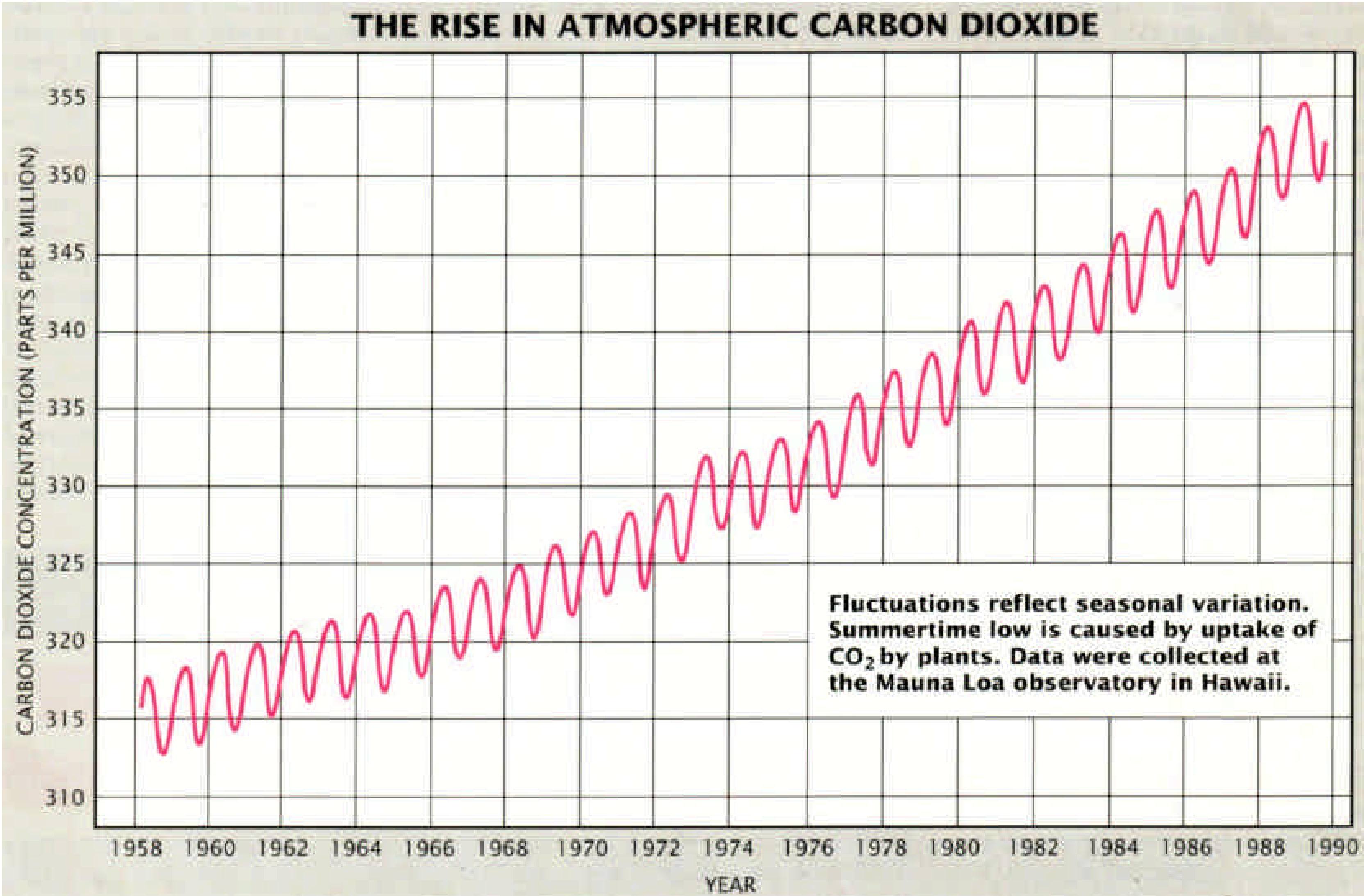
Ref.: Climate Change 1995, published by the IPCC

THE VOSTOK SENSATION



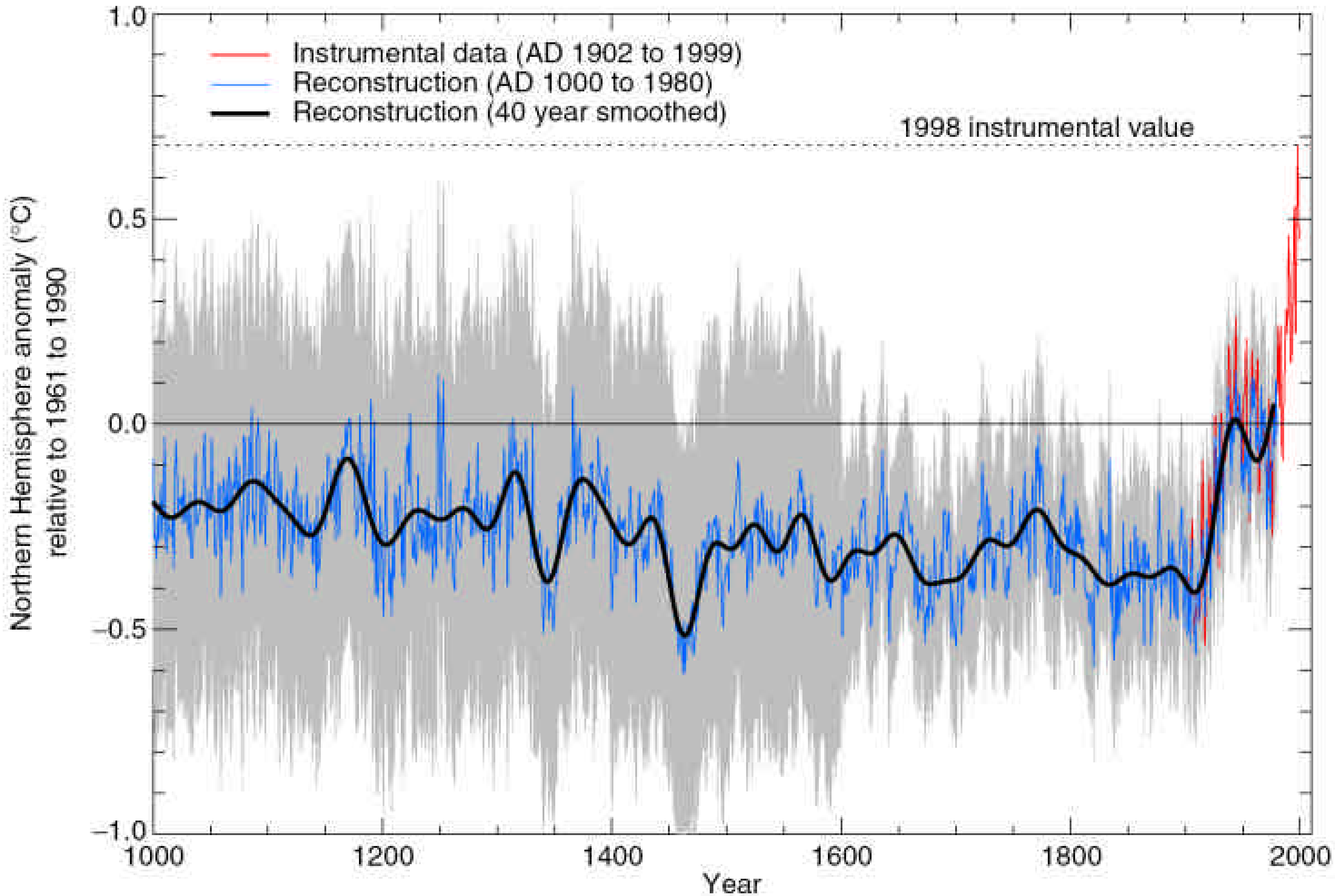
Petit, J.R.et al., „Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica." *Nature,* 399 (1999), pp. 429-436.

CO_2 CONCENTRATION IN THE ATMOPHERE



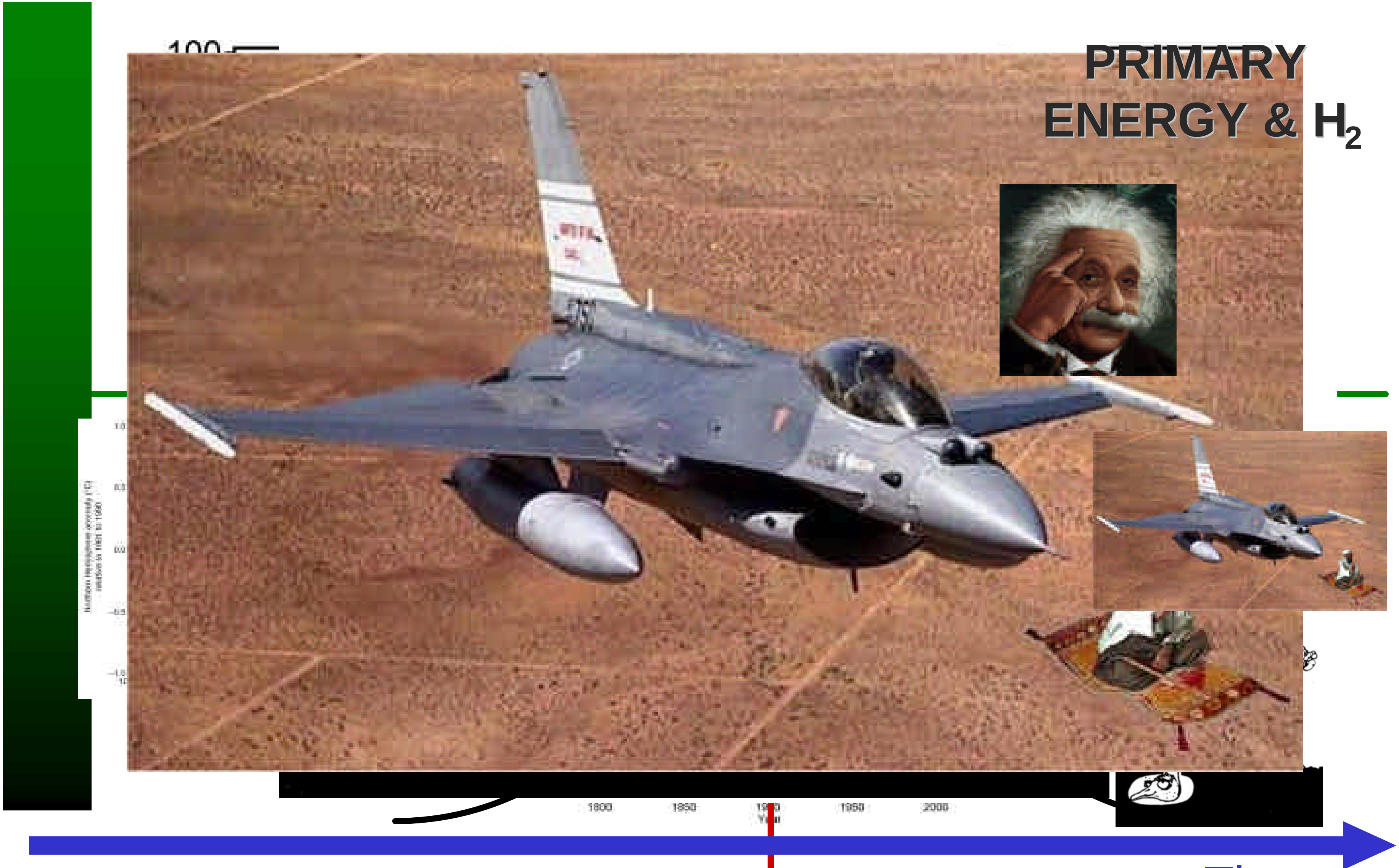
Ref.: Climate Change 2002, published by the IPCC

LONG TERM WORLD TEMPERATURE CHANGE



Millennial Northern Hemisphere (NH) temperature reconstruction (blue – tree rings, corals, ice cores, and historical records) and instrumental data (red). Ref.: Mann et al., Geophys. Res. Letters 26 (1999), pp. 759

ENERGY DEVELOPMENT



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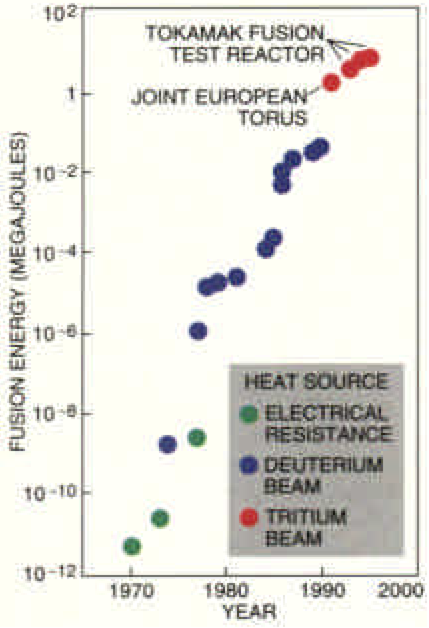
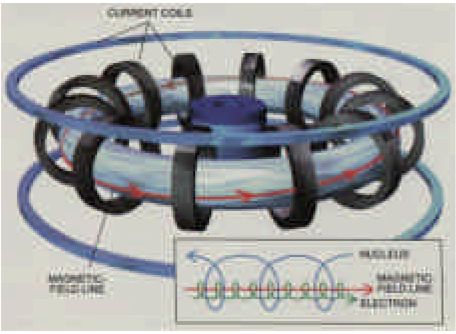
PRIMARY ENERGY

NUCLEAR FUSION

Lawson product: $\rho \cdot \tau \cdot T > 6 \cdot 10^{28}$ K s m^{-3}

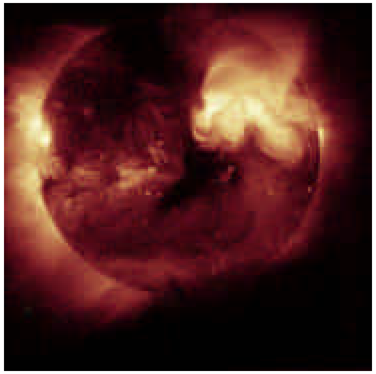


Terrestrical



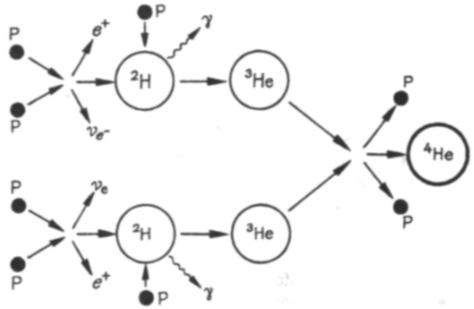
$$^{2}D + {}^{3}T \rightarrow {}^{4}He + n \text{ (17.6 MeV)}$$

Extraterrestrical (Sun, renewable energy)



$$4\,{}^{1}H + 2\,e^{-} \rightarrow {}^{4}He + 2\,\nu_e + 6\,h \cdot \nu \text{ (26 MeV)}$$

Solar constant = 1369 W m^{-2}



RENEWABLE ENERGY

WINDPOWER

HYDROPOWER

BIOMASS

SOLARTHERMAL POWER

PHOTOVOLTAICS

GEOTHERMAL ENERGY

WORLD ENERGY DEMAND

World energy consumption (2020): $140 \cdot 10^{12}$ kWh/year

- Solar constant: 1369 W/m^2
- 50% reaches the surface of the earth
- 50% is night
- Efficiency of photovoltaics: 10%.

Minimum surface area of photovoltaic cells:

473'000 km^2

or 80 m^2/person

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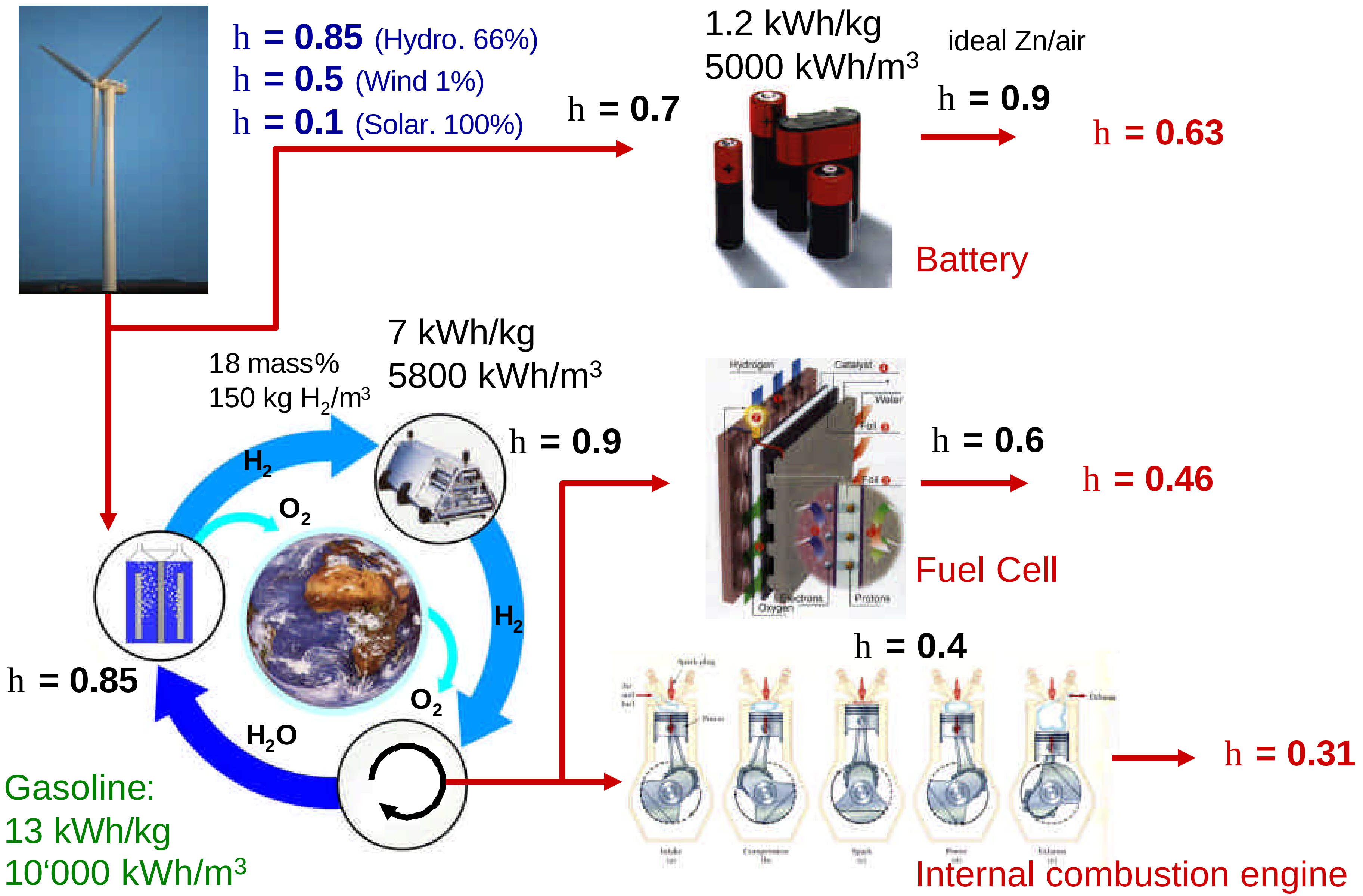
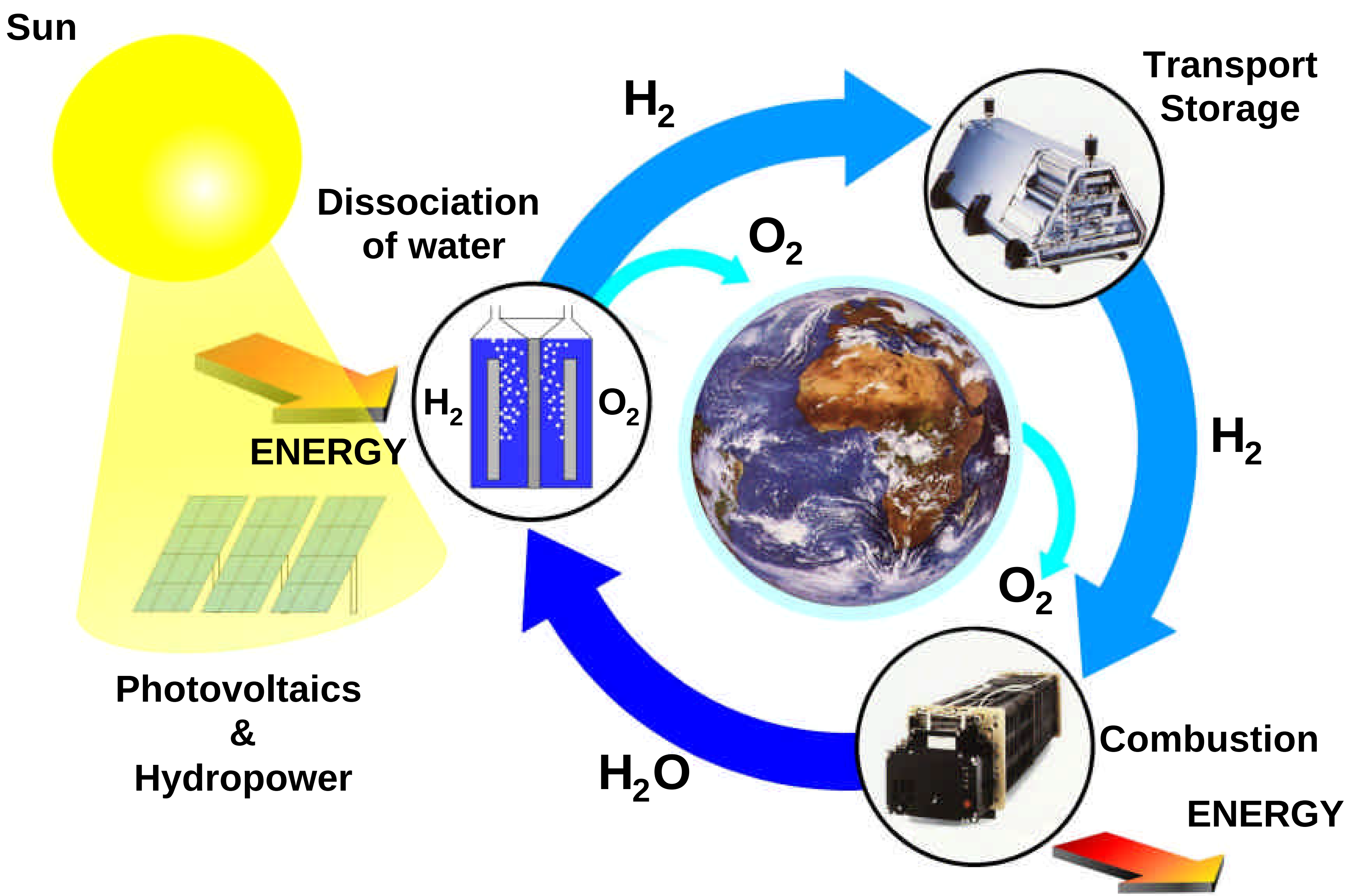
RENEWABLE ENERGY CONVERSION



HYDROGEN CYCLE



HYDROGEN PRODUCTION FROM FOSSIL FUELS

$-CH_2- + H_2O \longrightarrow 2\ H_2 + CO$

?H = 194 kJ ·mol^{-1}

$CO + H_2O \longrightarrow H_2 + CO_2$

?H = 2 kJ ·mol^{-1}

$H_2 + 0.5\ O_2 \longrightarrow H_2O$

?H = -285 kJ·mol^{-1}

Process	raw material	T [ºC]	p [bar]	catalyst	gas components
steam reforming	$- CH_2 -$, H_20	> 850	25	NiO	H_2, CO
plasma reforming	$- CH_2 -$, H_20	> 1350	3	-	H_2, CO
partial oxidation	$- CH_2 -$, H_20, O_2	> 1200	10-100	-	H_2, CO
coal gasification	C, H_20, O_2	800-1200	1-40	-	H_2, CO
CO conversion	CO, H_20	200-500	3	Fe_2O_3, Cr_2O_3	H_2, CO_2

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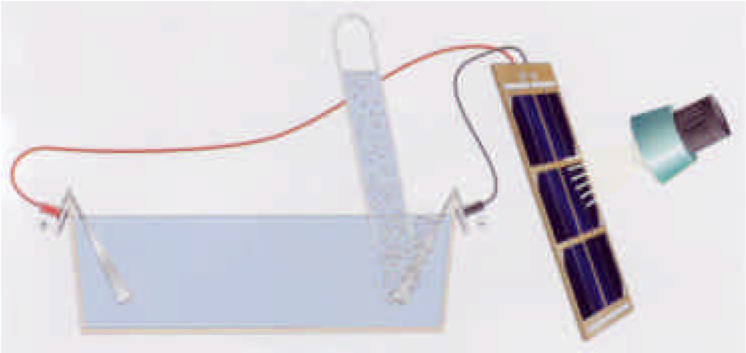
HYDROGEN PRODUCTION BY ELECTROLYSIS

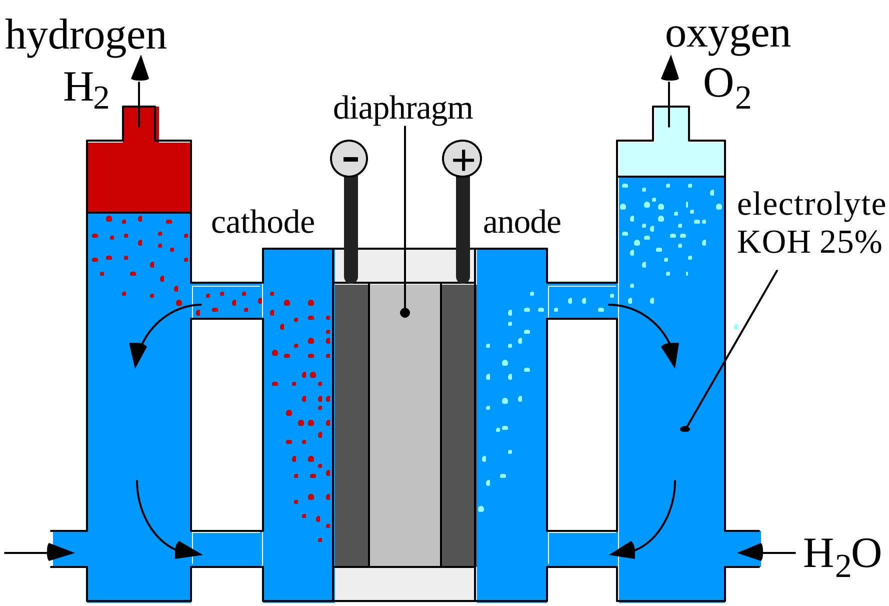


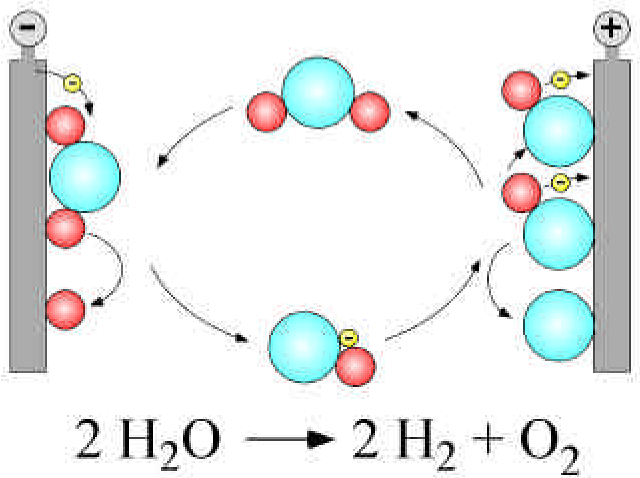
$$2\,OH^- + \rightarrow H_2O + e^- + O_{ad}$$

$$E^0 = +1.228\ V$$

$$H_2O + e^- \rightarrow OH^- + H_{ad}$$

$$E^0 = 0\ V$$





Cathode

Anode

HYDROGEN DISSOCIATION: THERMODYNAMICS

Cathode: $H_2O + e^- \rightarrow OH^- + H_{ad}$

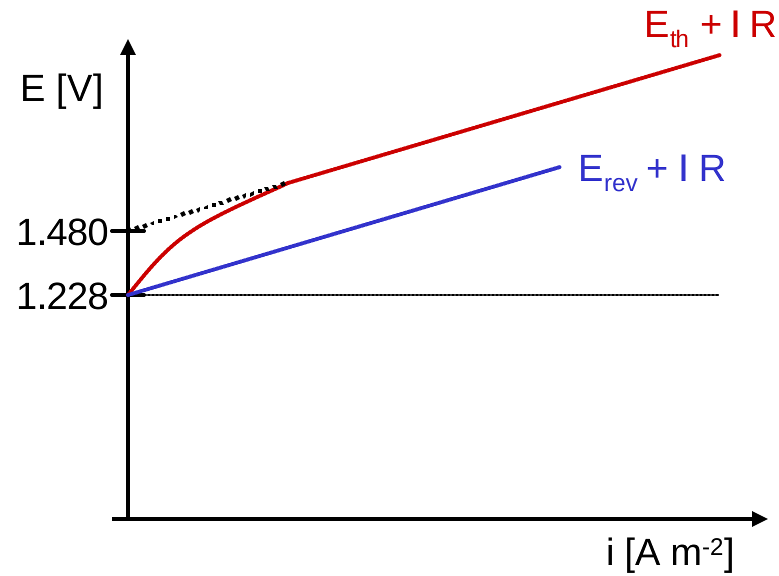
Anode: $2\ OH^- + \rightarrow H_2O + e^- + O_{ad}$

Cell reaction: $H_2O^{(liq)} \rightarrow H_2^{(g)} + ½\ O_2^{(g)}$

$\Delta H^0_{298K} = 286\ kJ\ mol^{-1}$

$\Delta S^0_{298K} = 163\ kJ\ K^{-1}\ mol^{-1}$

$\Delta G^0_{298K} = 237\ kJ\ mol^{-1}$



Enthalpy change:

$$\Delta H = \Delta G + T \cdot \Delta S = n \cdot F \cdot \left[-E + T \cdot \left(\frac{\partial E}{\partial T} \right)_p \right]$$

Gibbs free energy:

$W = \Delta G = n\ F\ E_{rev}$, $F = 96'495\ As\ mol^{-1}$

Pressure dependence of the potential:

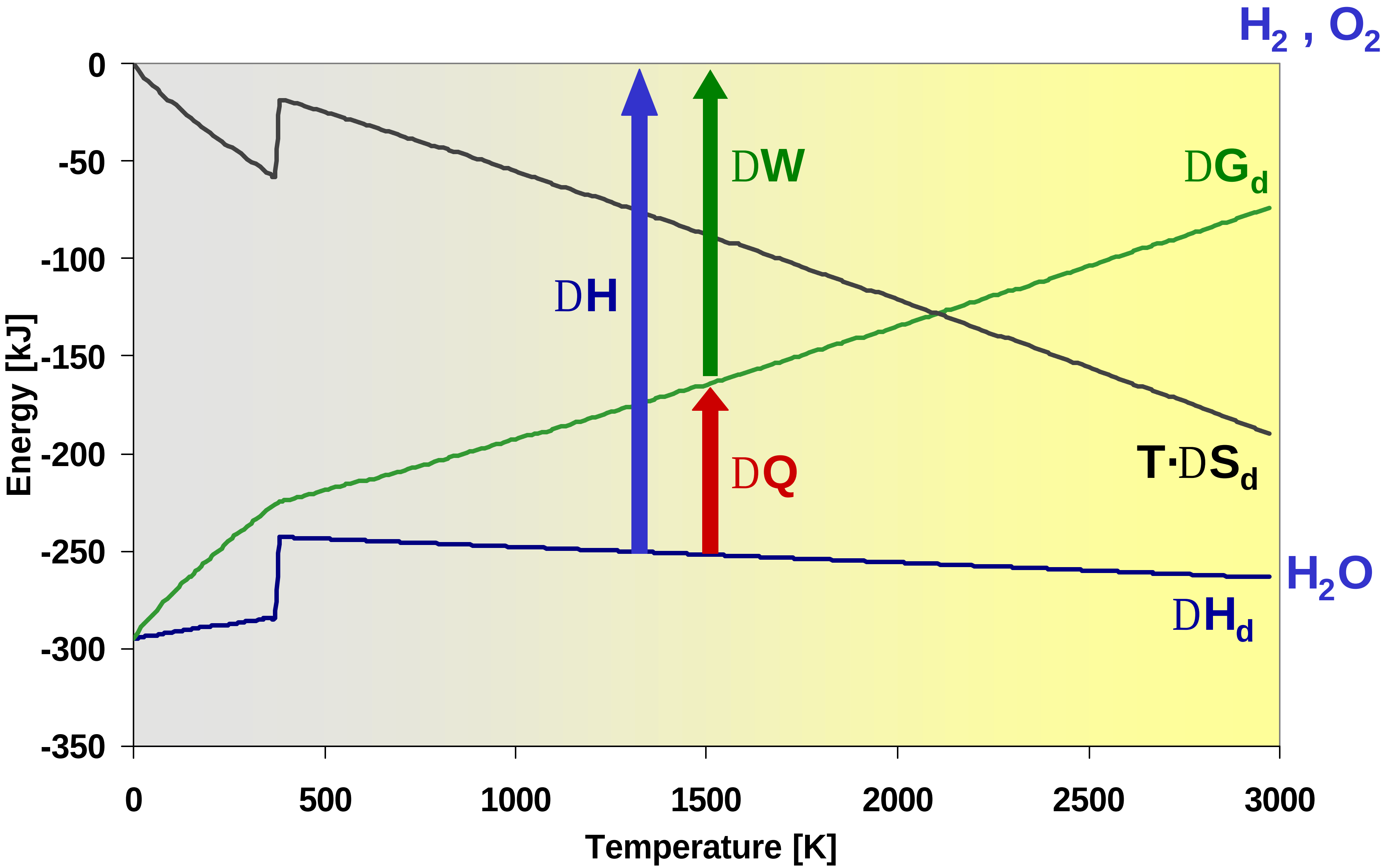
$$\Delta E_p = \Delta E^0 + \frac{R \cdot T}{2 \cdot F} \cdot \ln \left\{ \frac{p_{(H_2)} \cdot \sqrt{p_{(O_2)}}}{p^0} \right\}$$

$$\Delta E_p = \Delta E_{(p=p^0)} + 0.0189 \cdot \ln \left\{ \frac{p}{p^0} \right\}$$

Efficiency:

$$h_{rev} = \frac{\Delta G}{\Delta H} \qquad h = \frac{\Delta H}{W_{el}} = \frac{E + \frac{T \cdot \Delta S}{n \cdot F}}{U}$$

WATER DISSOCIATION H_2O ® H_2 + ½ O_2



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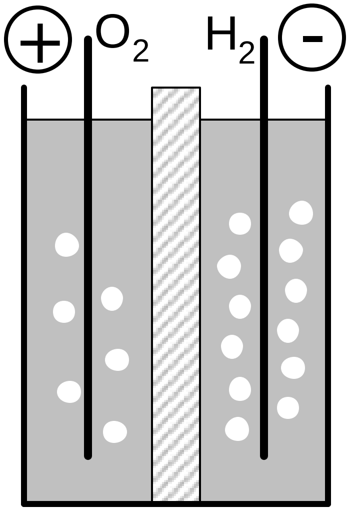
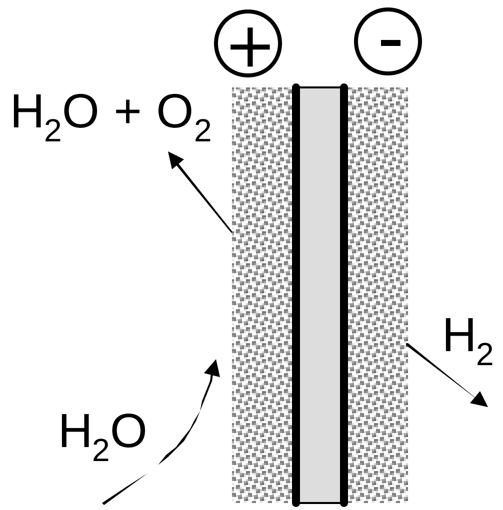
WATER ELECTROLYSIS

Diffusion Membran Electrolyser



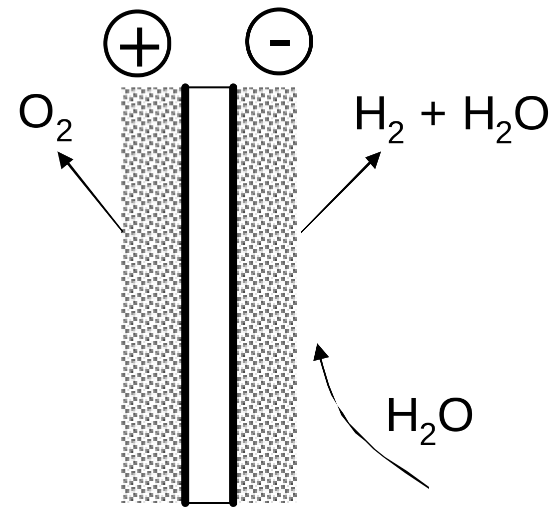
Membrane
30% KOH, 80°C

Polymer-Electrolyte (PEM) Electrolyser



Nafion® (H^+)
pure H_2O, 100°C

Solidoxid Electrolyte (SOE) Electrolyser



ZrO_2 (O^{2-})
H_2O steam at 800°C

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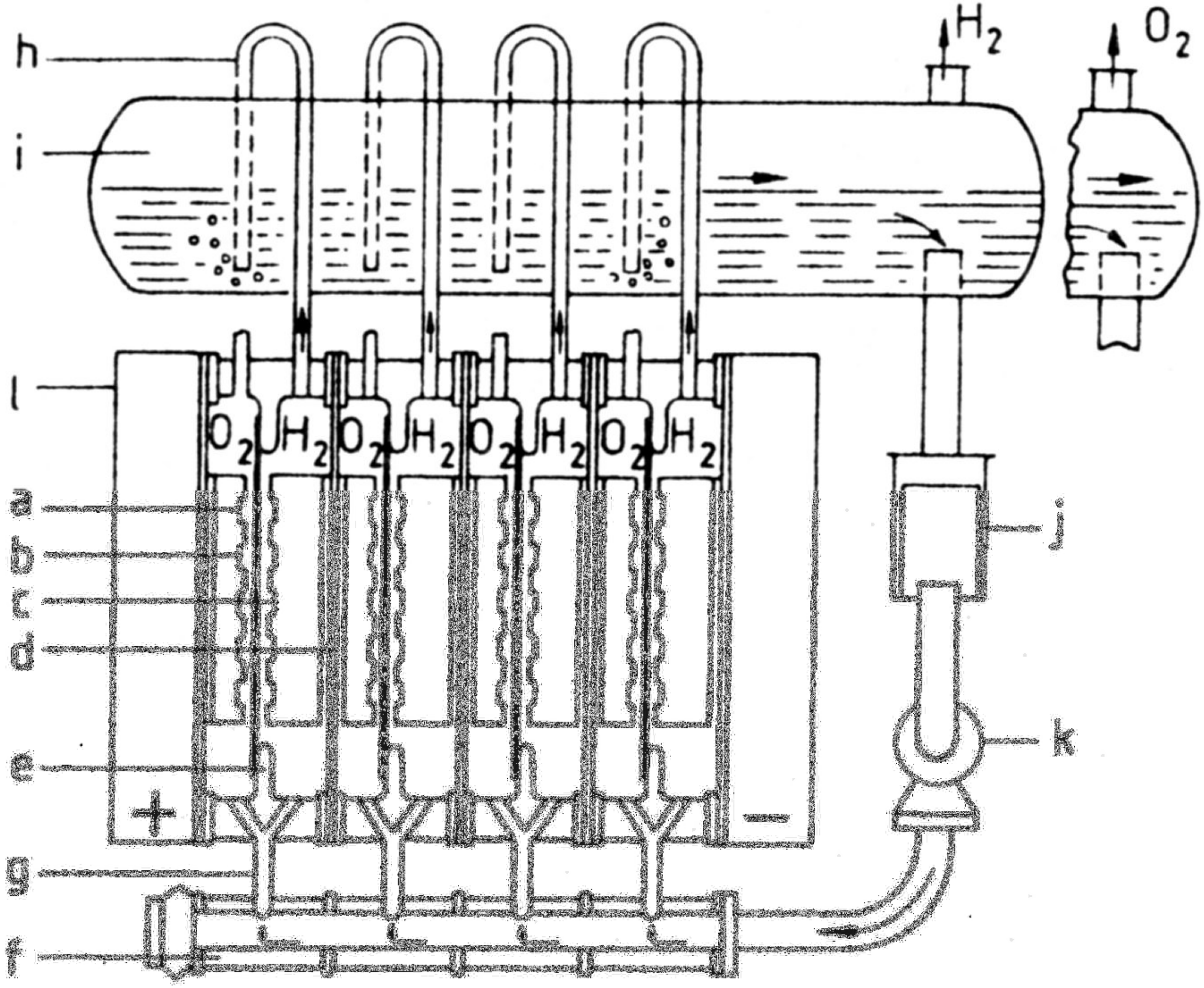
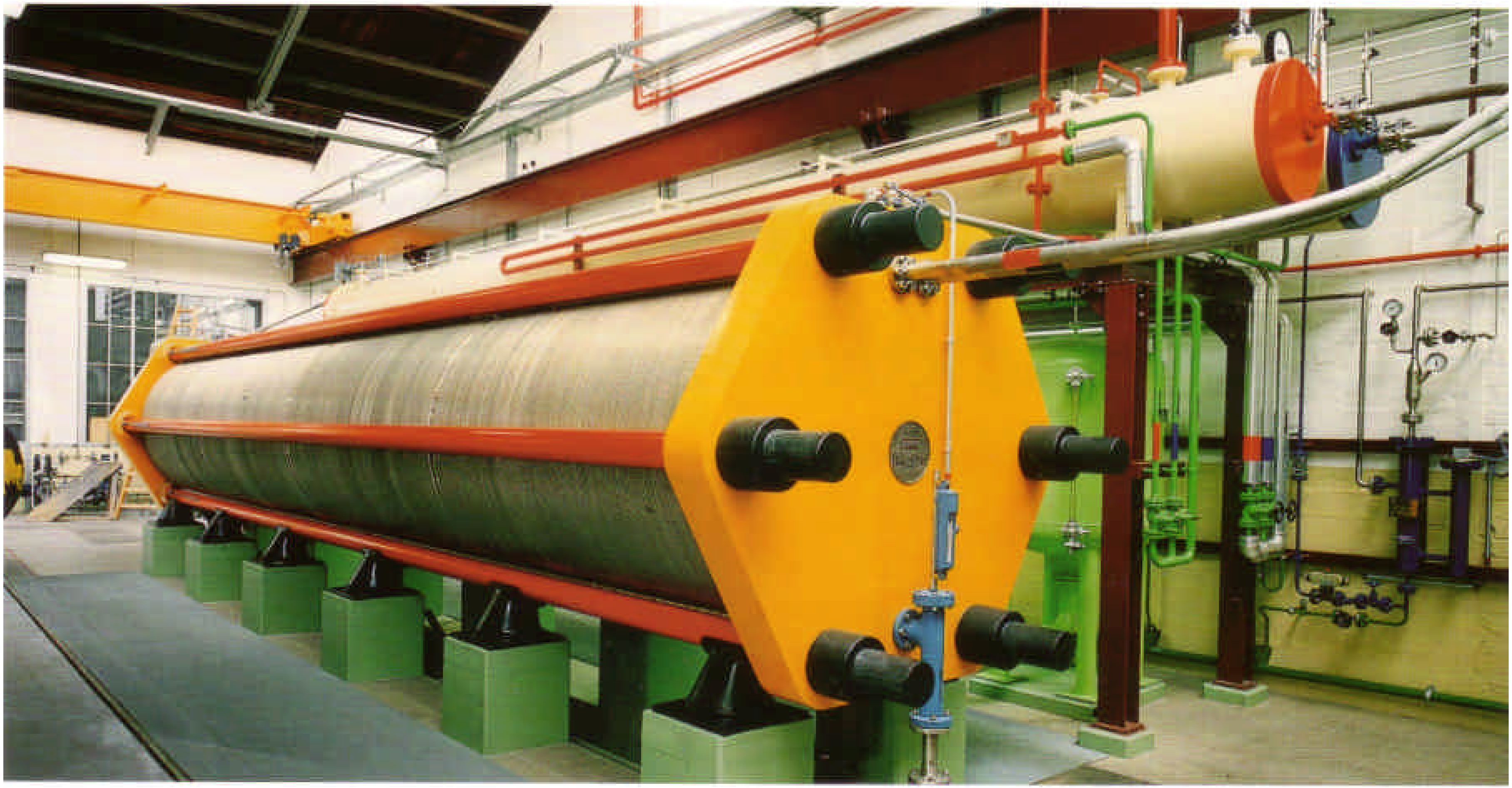
ELECTROLYSER



ELECTROLYSER



High pressure electrolyser (30 bar), 40‘000 $Nm^3 H_2$ per day (8 MW), Djeva, Giovanola, Jülich

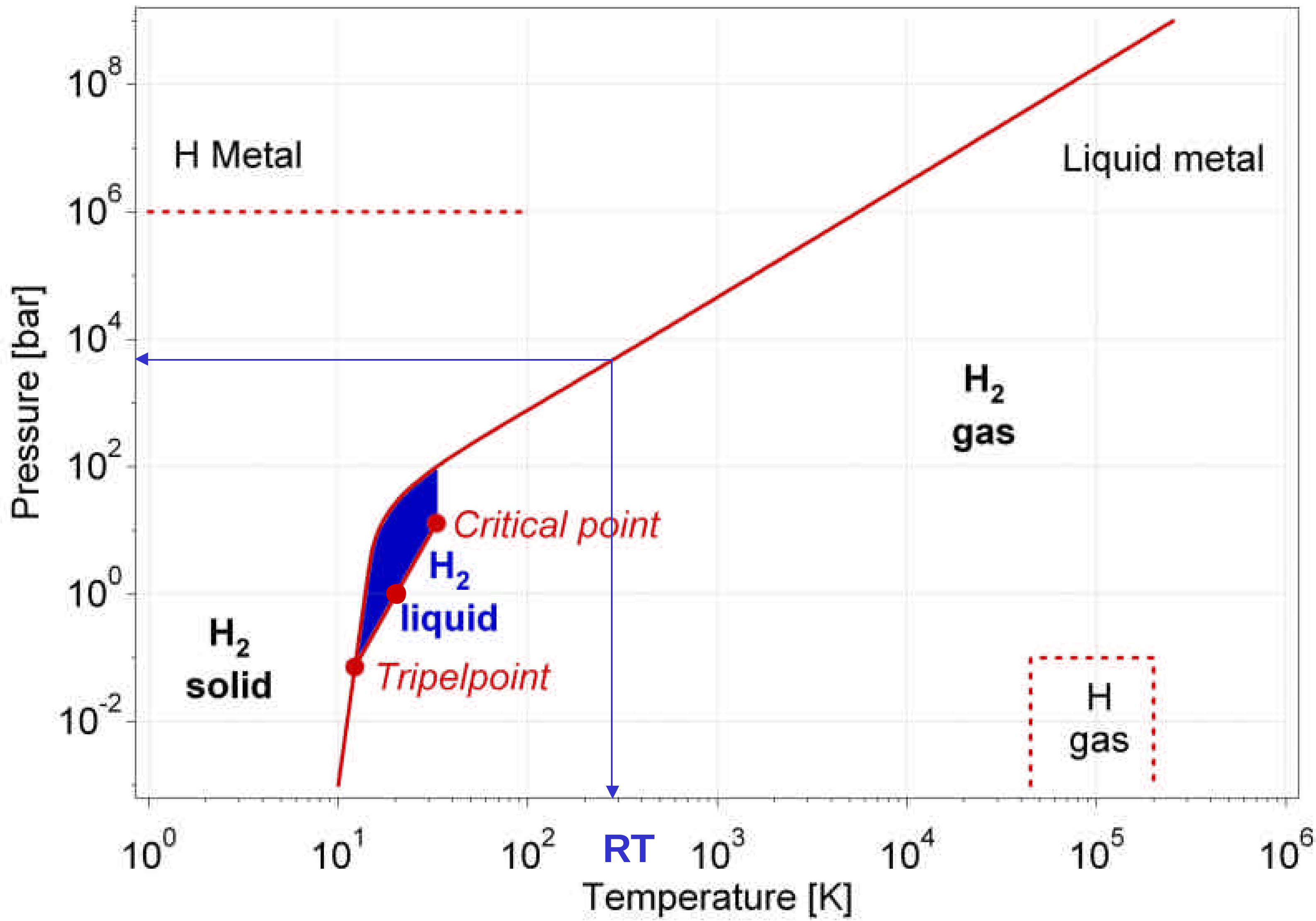
Technical data:

Voltage: 1.48 V (1.85 V)

Energy: 39.4 kWh/kg H_2 (49 kWh/kg H_2) (1 kg H_2 = 11.2 m^3 H_2 at 1 bar)

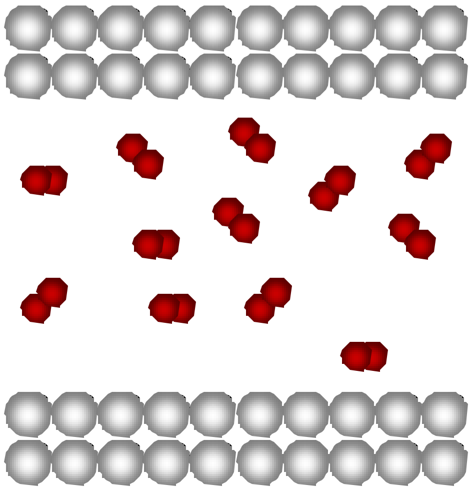
Efficiency: 80%

PRIMITIVE PHASEDIAGRAM OF HYDROGEN

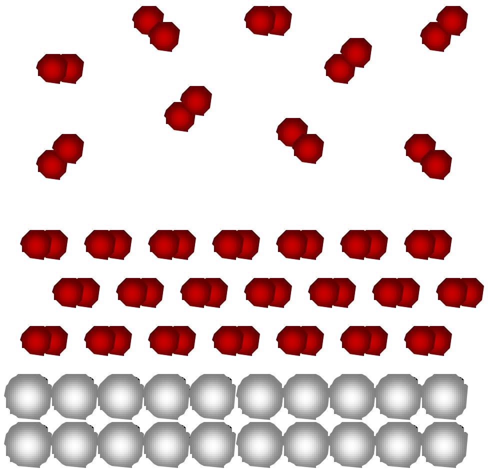


Ref: W. B. Leung, N. H. March and H. Motz, Physics Letters 56A (6) (1976), pp. 425-426

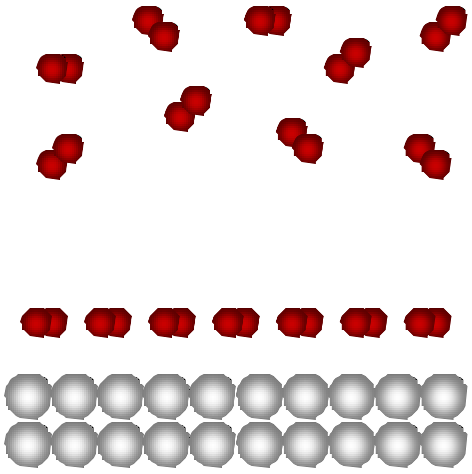
HYDROGEN STORAGE



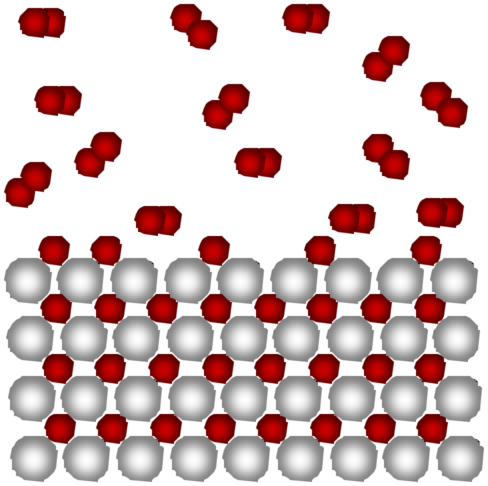
Hydrogen gas



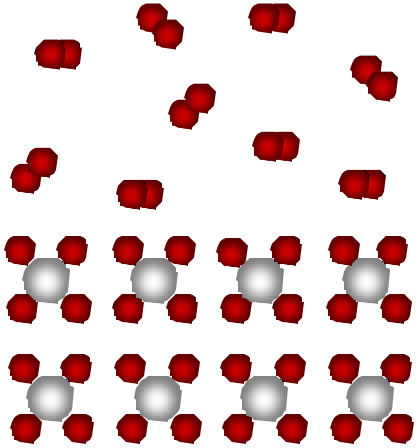
Liquid hydrogen



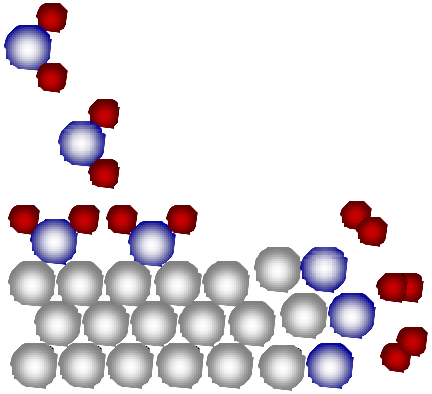
Physisorption



Metalhydride

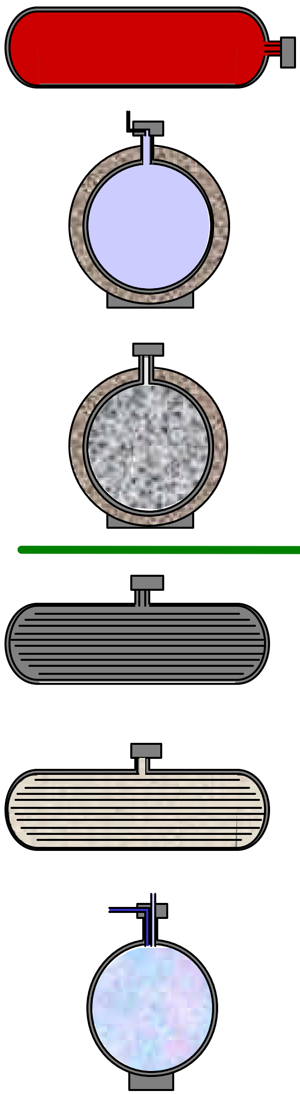


Complex hydrides



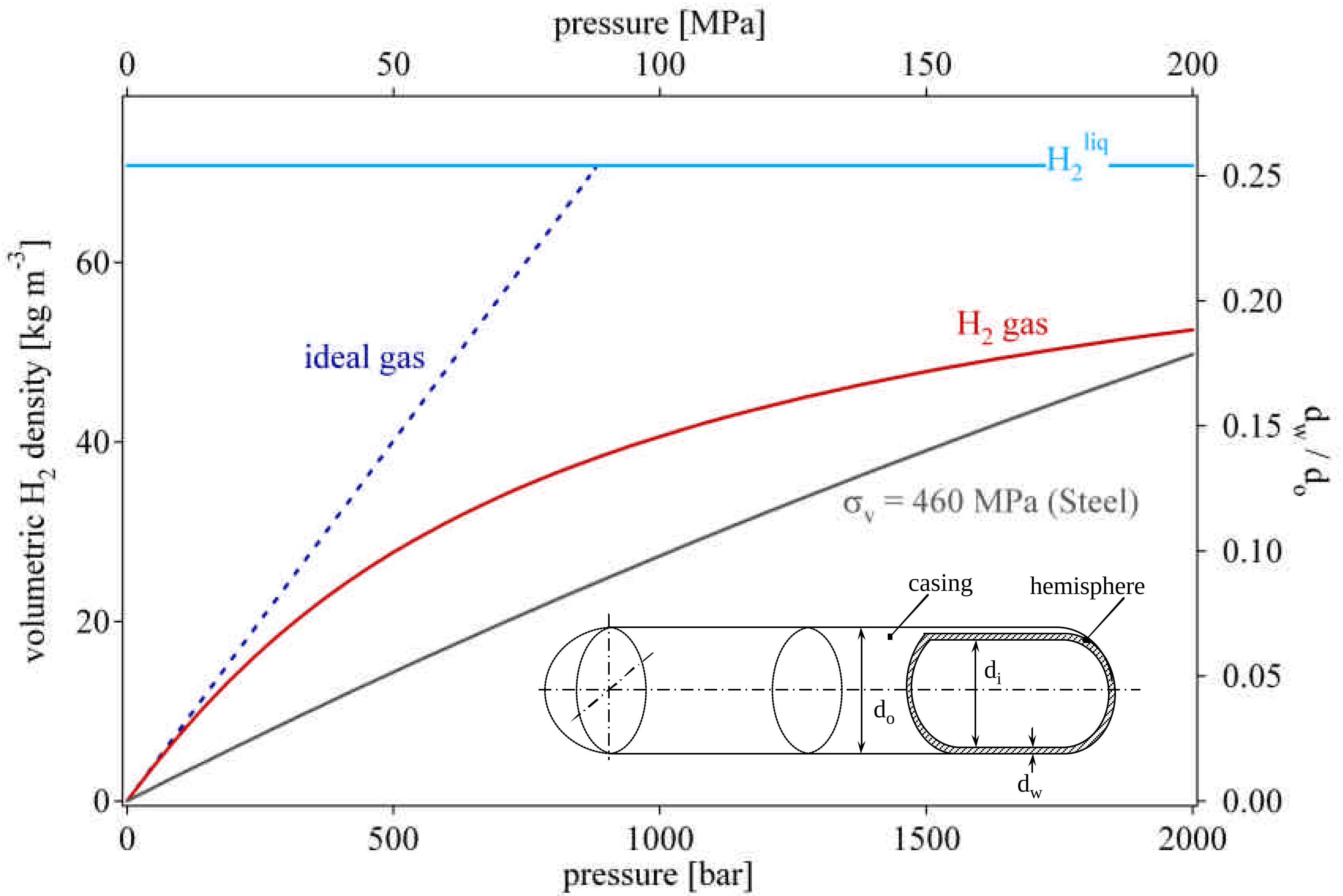
Chemical hydrides

HYDROGEN STORAGE



Storage Media		Volume	Mass	Pressure	Temperature	
	molecular H_2	max. 33 kg $H_2 \cdot m^{-3}$	13 mass%	800 bar	298 K	Composite cylind.
						established
		71 kg $H_2 \cdot m^{-3}$	100 mass%	1 bar	21 K	Liquid hydrogen
		20 kg $H_2 \cdot m^{-3}$	4 mass%	70 bar	65 K	Physisorption
	atomic H	max. 150 kg $H_2 \cdot m^{-3}$	2 mass%	1 bar	298 K	Metalhydrides
		150 kg $H_2 \cdot m^{-3}$	18 mass%	1 bar	298 K	Complex hydrides
						reversibility ?
		>100 kg $H_2 \cdot m^{-3}$	14 mass%	1 bar	298 K	Alkali + H_2O

PRESSURIZED HYDROGEN



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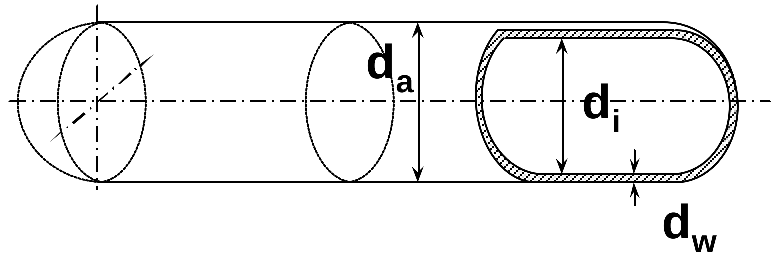
PRESSURE CYLINDER

$$\frac{d_w}{d_a} = \frac{\Delta p}{2 \cdot \sigma_v + \Delta p}$$

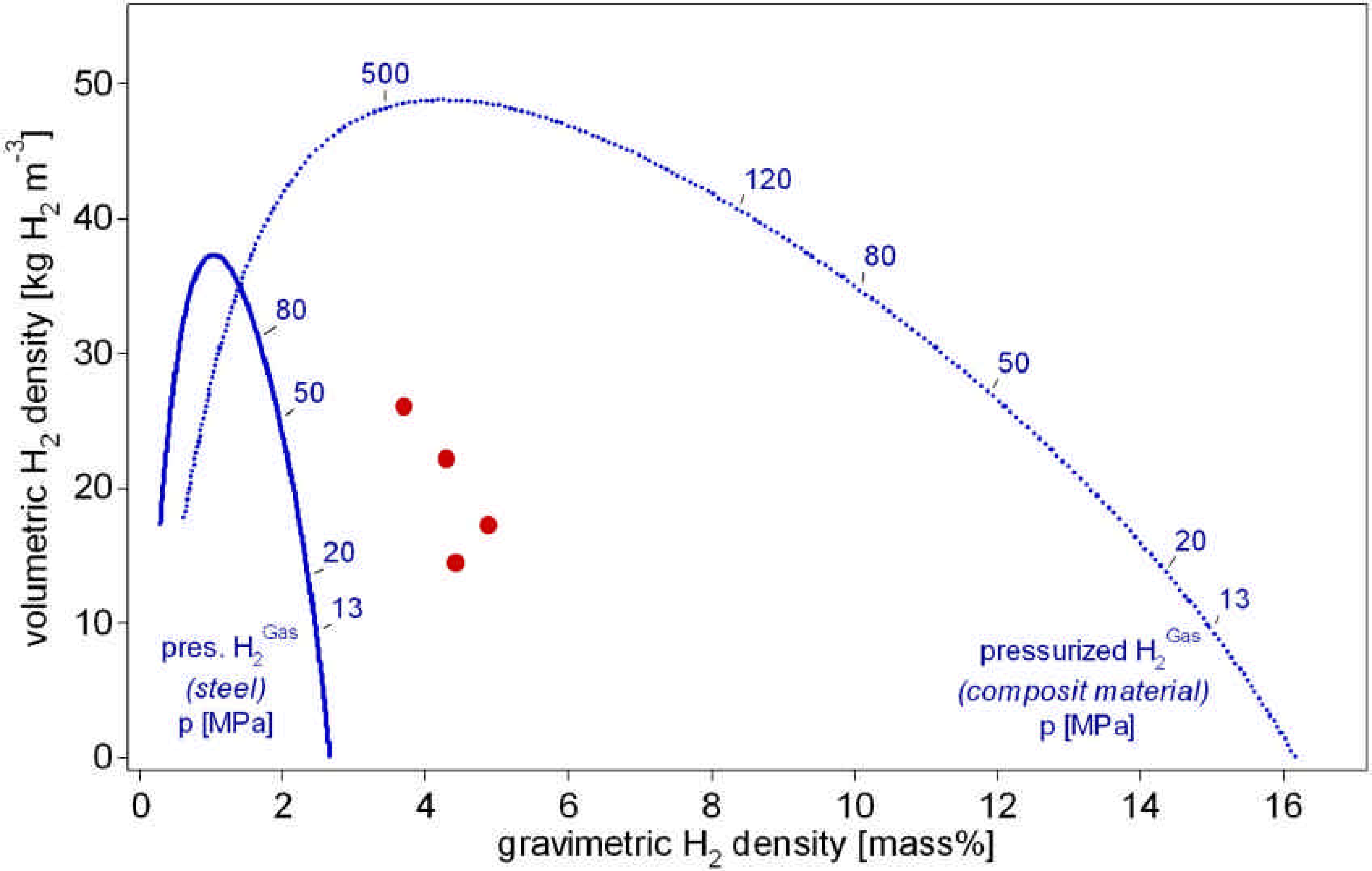


Material	density [g·cm^{-3}]	T_m [°C]	Youngs modulus [GPa]	tensile strength [MPa]
stainless steel AISI 304				
Fe/Cr18/Ni10	7.93	1400-1455	190-210	460-1100
stainless steel AISI 316				
Fe/Cr18/Ni10/Mo3	7.96	1370-1400	190-210	460-860
Cu	8.96	1083	129.8	224-314
Al	2.70	660.4	70.6	50-195
V	6.1	1890	127.6	260-730

L: low carbon, composition in %

Ref. http://www.goodfellow.com

HYDROGEN STORAGE DENSITY



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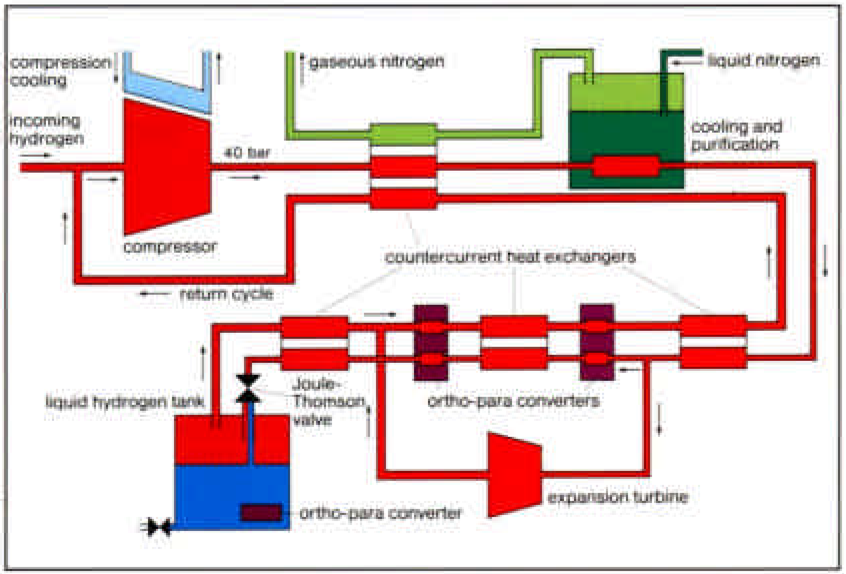
LIQUID HYDROGEN



Claude process for liquefying hydrogen

Energy use for liquefaction:

W_{th} = 3.92 kWh·kg^{-1}

W_{prac} = 10 kWh·kg^{-1}

Density (H_2 liq.) = 70.8 kg·m^{-3}

Plant for liquefying hydrogen (Linde)

75% Orthohydrogen

at RT

25% Parahydrogen

ΔH(T<77K)
523 kJ·kg^{-1}

ΔH_{vap}(T=21.2K)
452 kJ·kg^{-1}

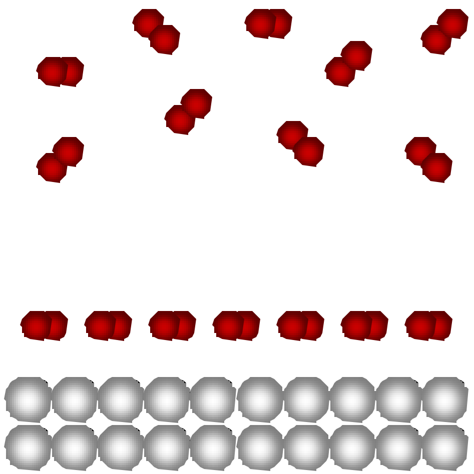
AIR AND SPACE APPLICATION

Tupolev 155 (1988), one engine on H_2

Space Shuttle
1535 m^3 liq. H_2, 120t

HYDROGEN STORAGE

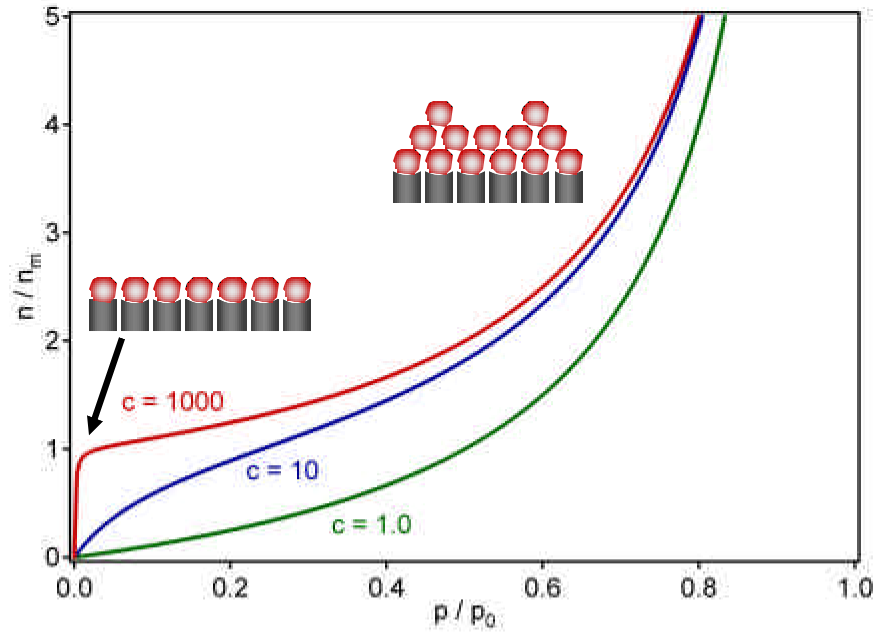
Physisorption

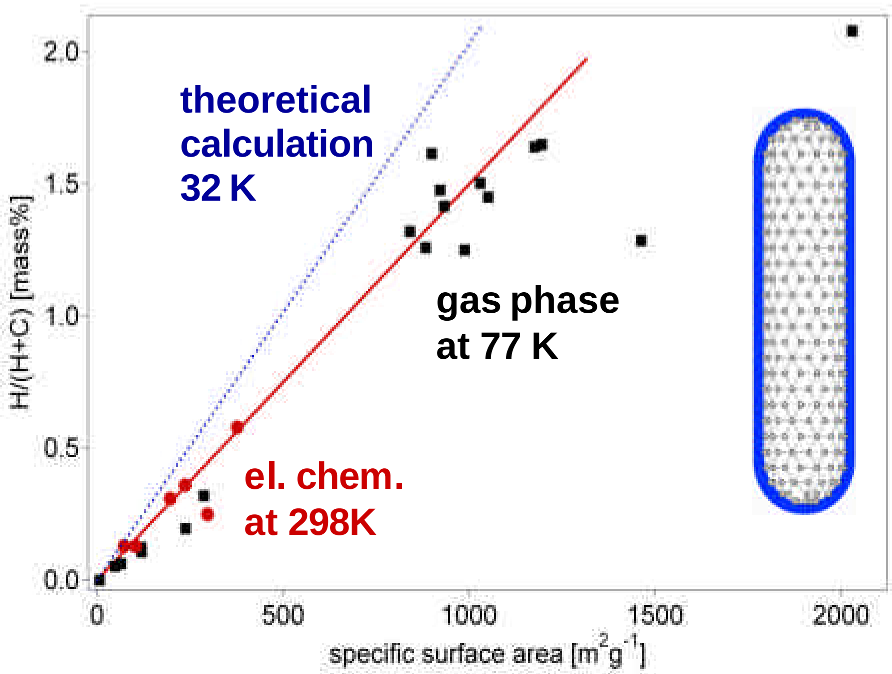


$$\frac{n}{n_m} = \frac{c \cdot \beta}{(1-\beta)\cdot(1+(c-1)\cdot\beta)}$$

$$\beta = F \cdot \frac{k_a^0}{k_d^0} e^{\frac{\Delta H_V}{k \cdot T}} = \frac{p}{p_0} \qquad c = e^{\frac{\Delta H_{ads} - \Delta H_V}{k \cdot T}}$$

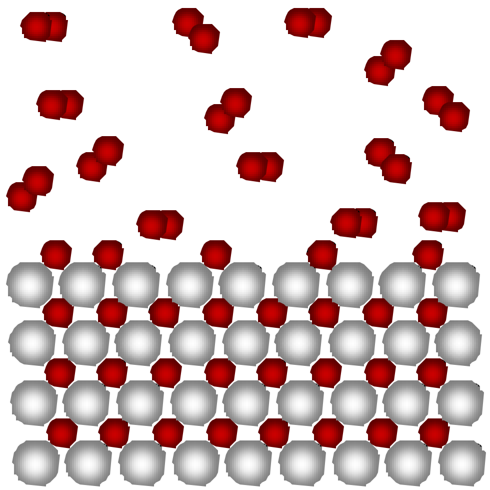
Ref.: A. Züttel et al., Int. J. of Hydrogen Energy 27 (2002), pp. 203-212
M.G. Nijkamp et al., Appl. Phys. A 72 (2001), pp. 619–623
S. Brunauer, P. H. Emmett und E. Teller, J. Amer. Chem. Soc. 60 (1938), p. 309





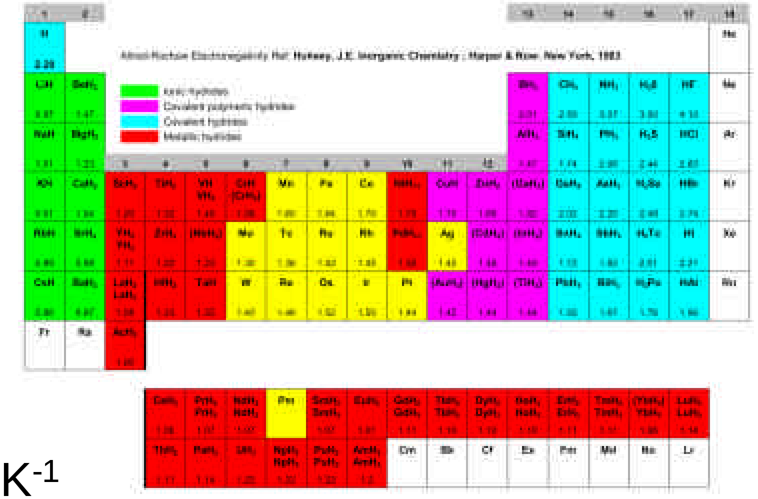
HYDROGEN STORAGE

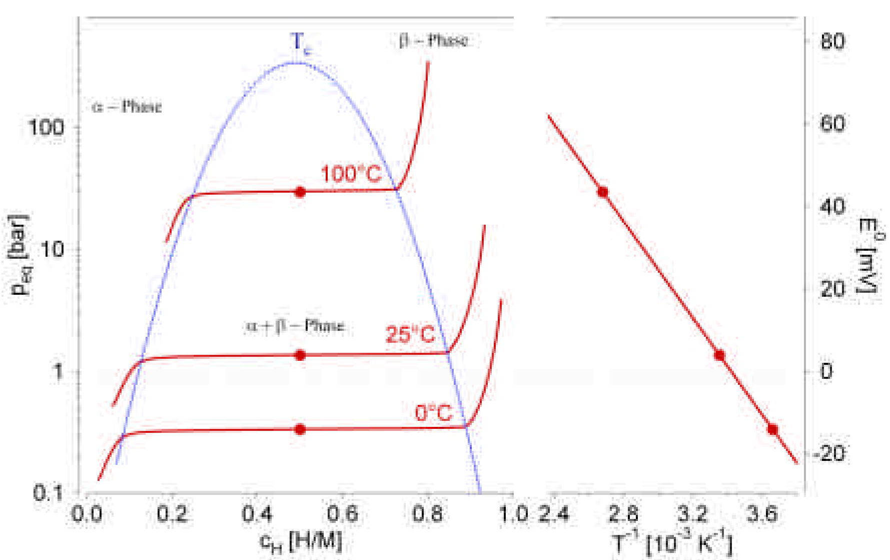
Metalhydride

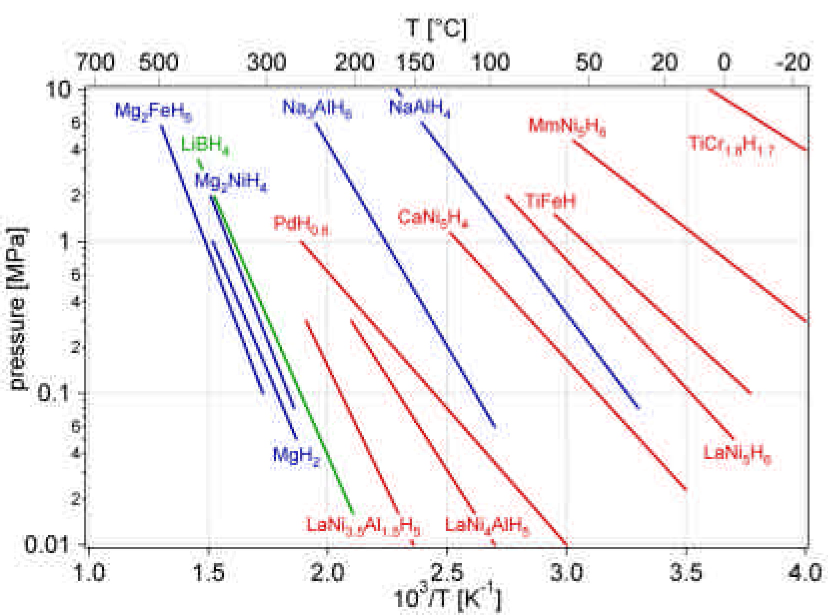


$\rho_V < 150\ \mathrm{kg\ m^{-3}}$

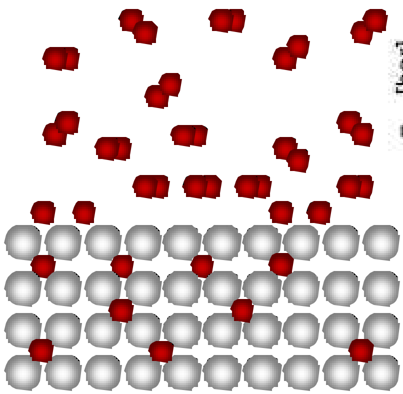
$S^0(H_2) = 130\ \mathrm{J\ mol^{-1}K^{-1}}$

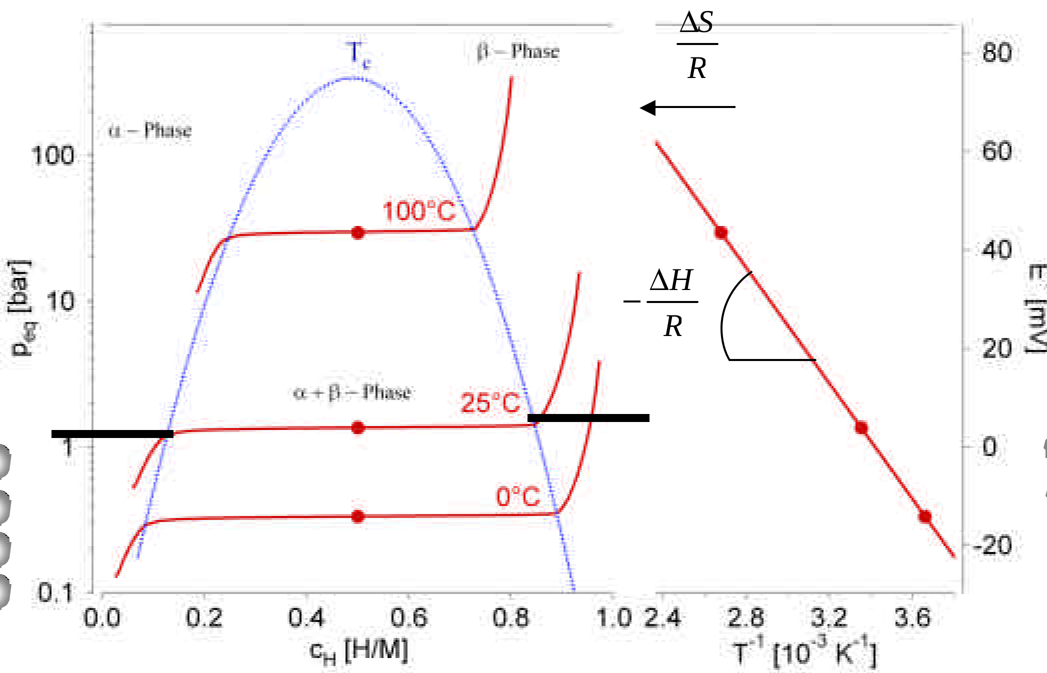


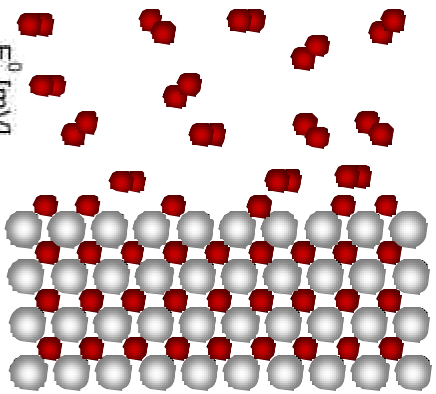




HYDROGEN ABSORPTION IN METALS







$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R\cdot T} + \frac{\Delta S^0}{R}$$

α-Phase: Solid Solution

MH_x (0 < x < 0.1)

~~H ↔ H~~, $\Delta V/V = k\cdot c_H$

β-Phase: Hydride Phase

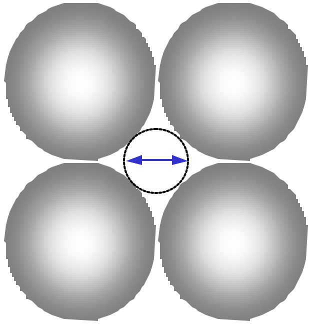
MH_x x = {1, 2, 3,…}

H ↔ H

EMPIRICAL MODELS: GEOMETRY

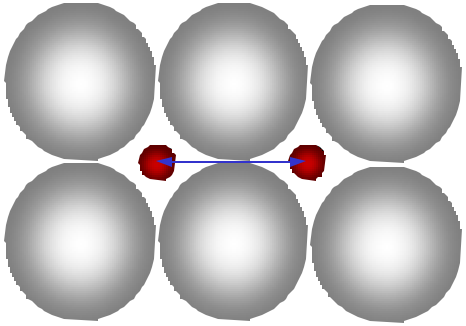
1) **Size of interstitial site:**

$r > 0.37$ Å



Westlake criterion

Ref.: D. G. Westlake, J. Less-Common Metals **91** (1983), pp.275-292



2) **Distance between hydrogen atoms:**

$d > 2.1$ Å

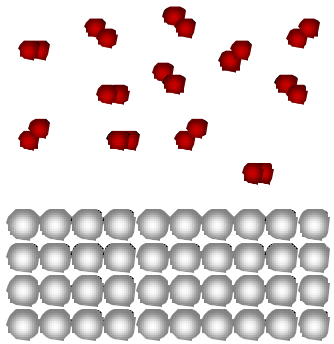
Ref.: A. C. Switendick, Z. Phys. Chem. N.F. 117 (1979), pp. 89

$\rho_V < 245\ \text{kg m}^{-3}$

Number of hydrogen atoms:

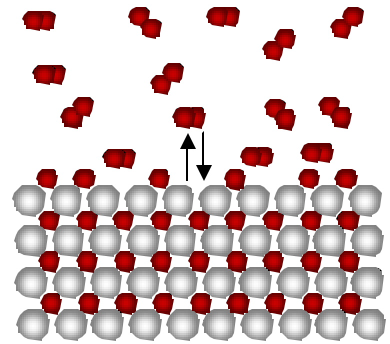
Number of interstitial sites for which 1) and 2) applies.

THERMODYNAMICS OF HYDRIDES



$\Delta H^0 < 0$
$\Delta S^0 < 0$
$\longrightarrow$

p



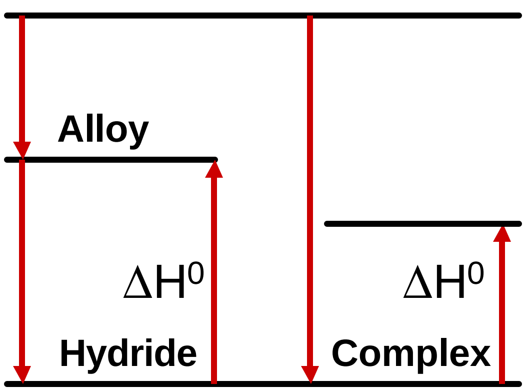
$$x\,M + H_2 \longrightarrow x\,MH_{2/x}$$

Equilibrium $\Delta G = 0$

$$G_{MH} - G_{H_2} = \Delta G = 0 = \Delta G^0 - R \cdot T \cdot \mathit{ln}\left(\frac{p}{p_0}\right)$$

$$\Delta G^0 = R \cdot T \cdot \mathit{ln}\left(\frac{p}{p_0}\right) = \Delta H^0 - T \cdot \Delta S^0$$

$$\mathit{ln}\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$



for $p = p_0$

$$T_{dec} = \frac{\Delta H^0}{\Delta S^0}$$

per H_2

$$\Delta S^0 = S^0(H_2) = 130\ \mathrm{J\ K\ mol^{-1}}$$

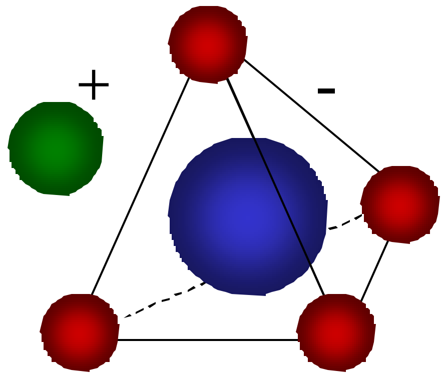
HYDRIDES

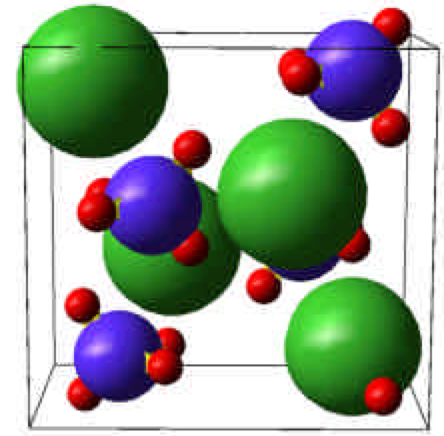
$$T_{dec} = \frac{\Delta H^0_{dec}(H_2)}{S^0(H_2)}$$

Material	H_2 [mass%]	T_{dec} [°C] 1 bar
$LaNi_5H_6$	1.49	15
$TiMn_{1.5}H_{2.5}$	1.76	-61
$FeTiH_2$	1.86	-10
ZrH_2	2.16	696
$TiCr_{1.8}H_{3.5}$	2.43	-120
Mg_2NiH_4	3.62	300
VH_2	3.81	-10,
TiH_2	3.98	780
NaH	4.20	430
CaH_2	4.79	1000
$Li_2NH + LiH$	5.50	600
$LiNH_2 + LiH$	6.50	300
$NaAlH_4$	7.46	30, 120
MgH_2	7.66	320
AlH_3	10.07	<RT
$LiAlH_4$	10.62	-93
$NaBH_4$	10.66	620
LiH	12.86	900
$Al(BH_4)_3$	16.90	<100
NH_3	17.75	-32
$LiBH_4$	18.51	230

Andreas Züttel, IfRES (2005)

COMPLEX HYDRIDES





1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
Li 0.97	Be 1.47											B 2.01	C 2.50	N 3.07	O 3.50	F 4.10	Ne
Na 1.01	Mg 1.23											Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83	Ar
K 0.91	Ca 1.04	Sc 1.20	Ti 1.32	V 1.45	Cr 1.56	Mn 1.60	Fe 1.64	Co 1.70	Ni 1.75	Cu 1.75	Zn 1.66	Ga 1.82	Ge 2.02	As 2.20	Se 2.48	Br 2.74	Kr
Rb 0.89	Sr 0.99	Y 1.11	Zr 1.22	Nb 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	Pd 1.35	Ag 1.42	Cd 1.46	In 1.49	Sn 1.72	Sb 1.82	Te 2.01	I 2.21	Xe
Cs 0.86	Ba 0.97	La 1.08	Hf 1.23	Ta 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	Au 1.42	Hg 1.44	Tl 1.44	Pb 1.55	Bi 1.67	Po 1.76	At 1.90	Rn
Fr	Ra	Ac 1.00															
			Ce 1.06	Pr 1.07	Nd 1.07	Pm	Sm 1.07	Eu 1.01	Gd 1.11	Tb 1.10	Dy 1.10	Ho 1.10	Er 1.11	Tm 1.11	Yb 1.06	Lu 1.14	
			Th 1.11	Pa 1.14	U 1.22	Np 1.22	Pu 1.22	Am 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

Examples:

$NaAlH_4$

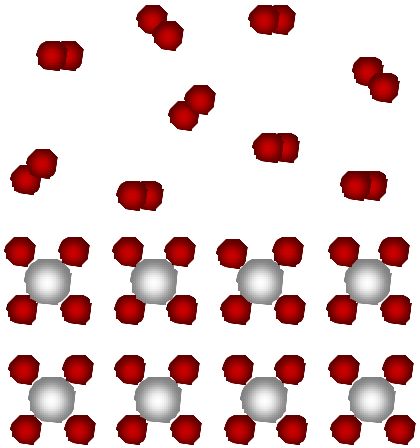
$Mg(AlH_4)_2$

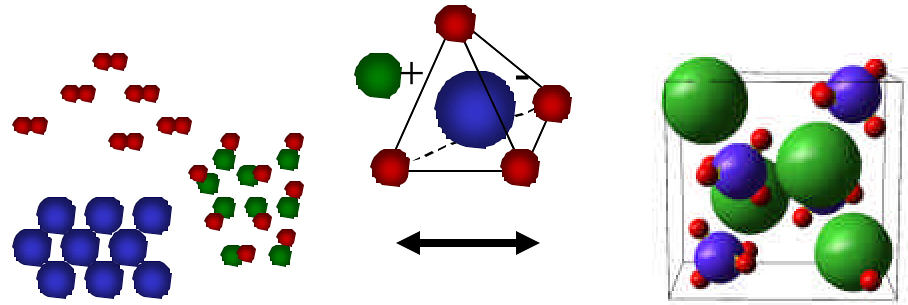
$LiBH_4$

$Mg(BH_4)_2$

$Al(BH_4)_3$

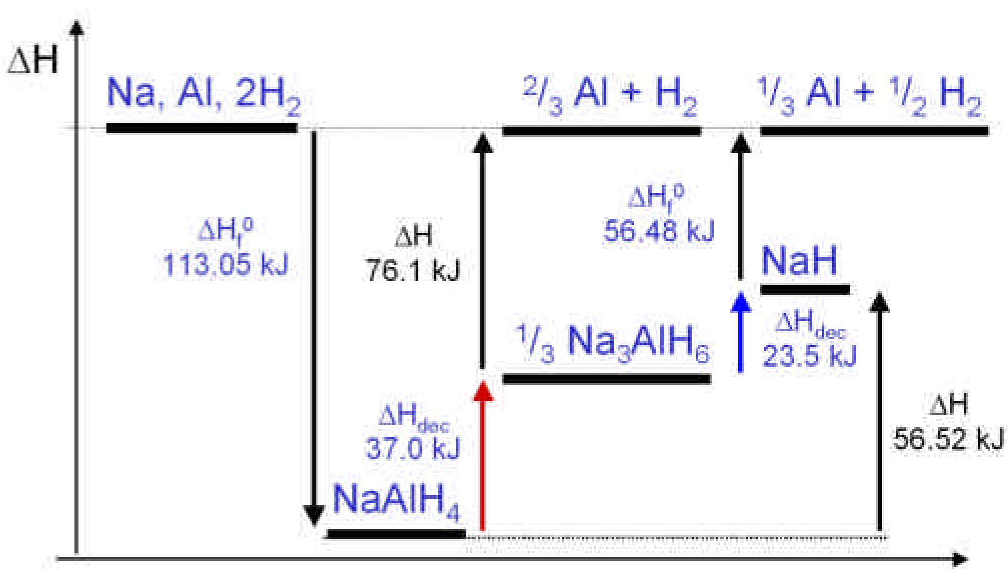
COMPLEX HYDRIDES

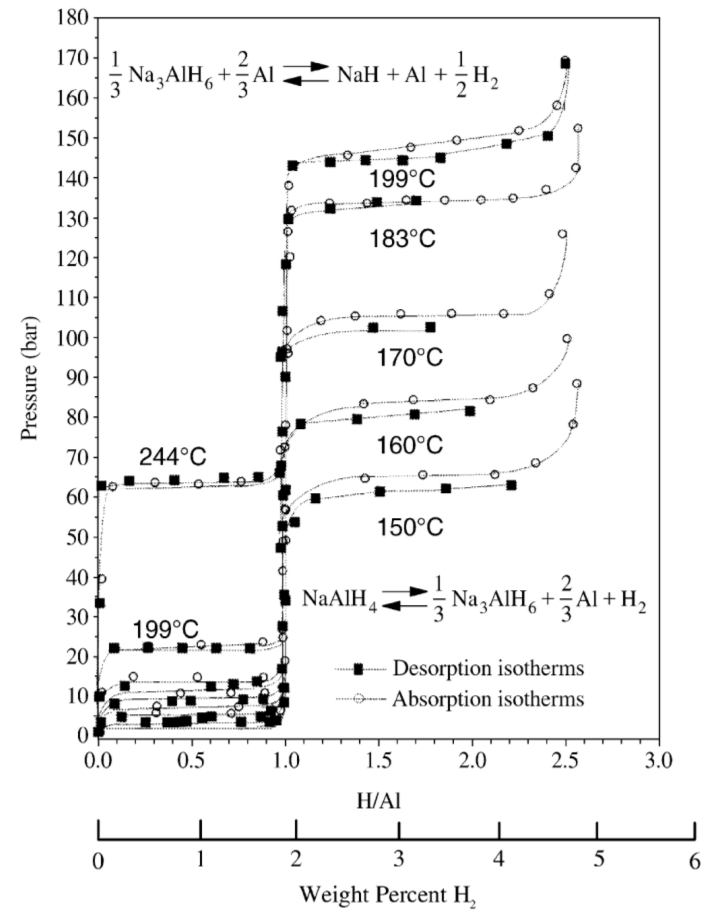




$$T_{dec}(p = p_0) = \frac{\Delta H^0}{\Delta S^0}$$

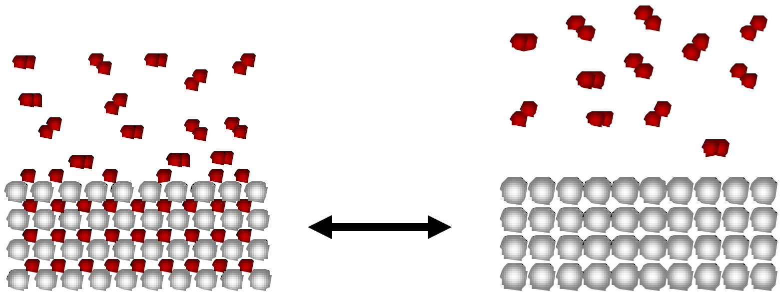
$NaAlH_4 \rightarrow \frac{1}{3} Na_3AlH_6 + \frac{2}{3} Al + H_2 \rightarrow Al + NaH + \frac{3}{2} H_2$

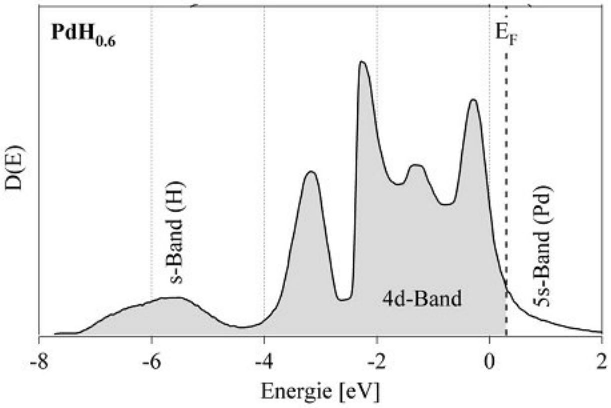




Ref.: B. Bogdanovic et al., J. Alloys and Comp. 302 (2000), pp. 36-58

METAL HYDRIDES

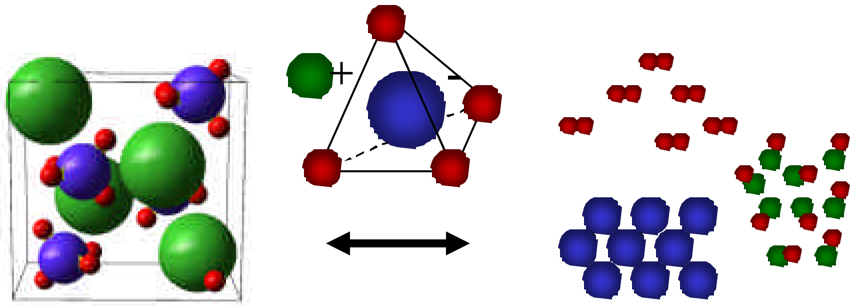


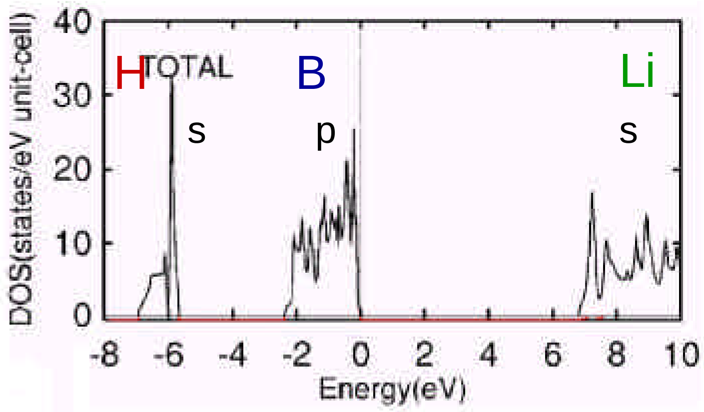


$$x\,MH_{2/x} \longrightarrow x\,M + H_2$$

$$ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

COMPLEX HYDRIDES



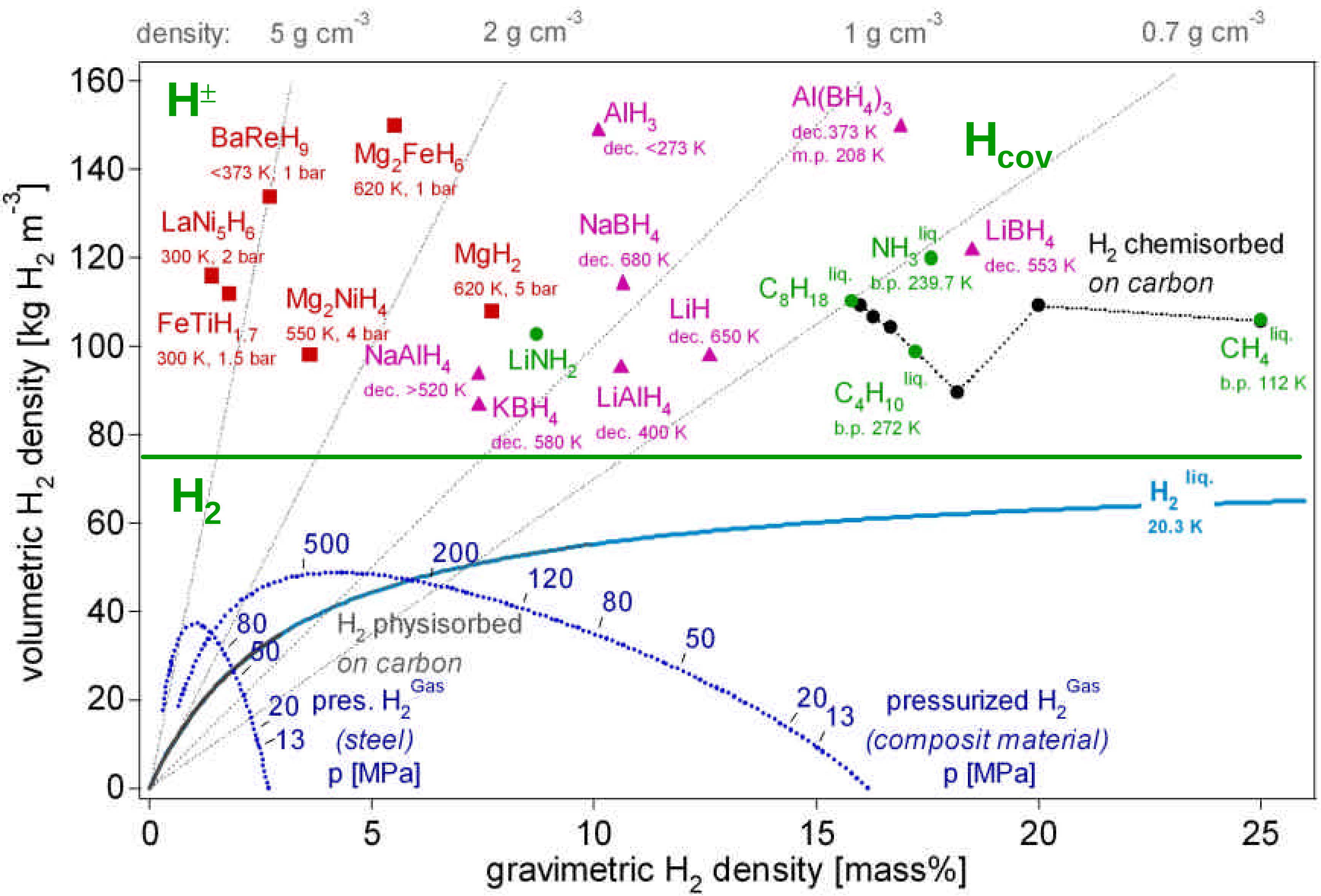


Ref. K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, Phys. Rev. B 69 (2004), 245120

$$^2/_3\,ABH_4 \longrightarrow {}^2/_3\,AH + {}^2/_3\,B + H_2$$

$$T_{dec}(p = p_0) = \frac{\Delta H^0}{\Delta S^0}$$

HYDROGEN DENSITY

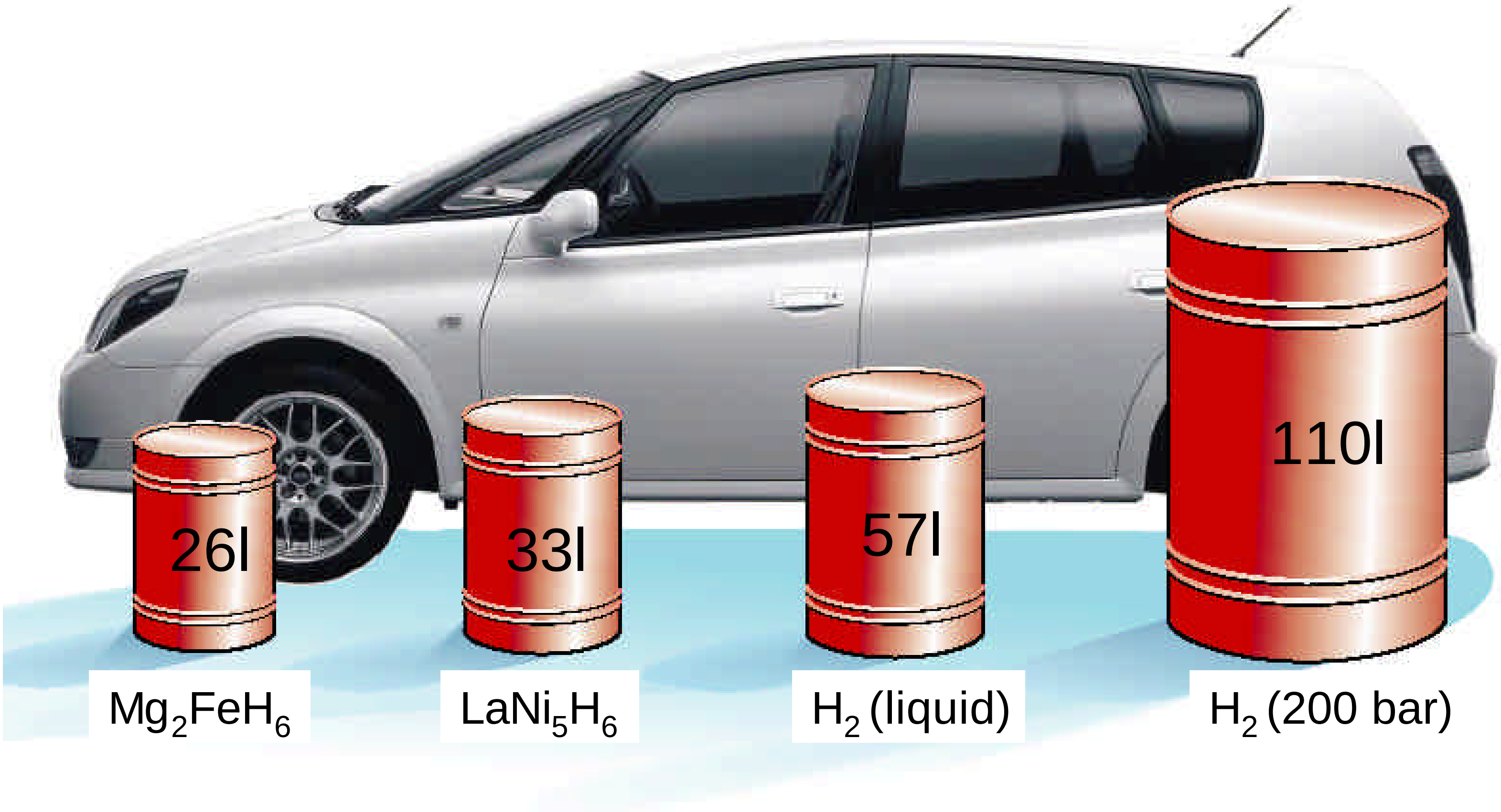


Ref: A. Züttel, “Materials for hydrogen storage”, materialstoday, Septemper (2003), pp. 18-27

VOLUME OF HYDROGEN STORAGE

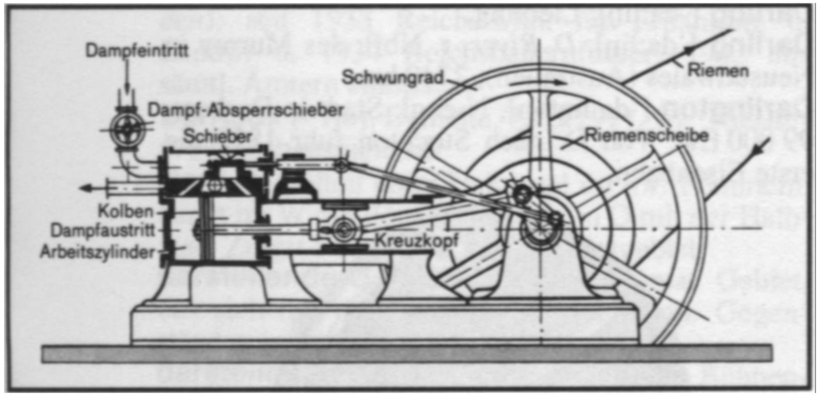
4 kg hydrogen

3 l gasoline / 100 km = 0.3 kWh / km

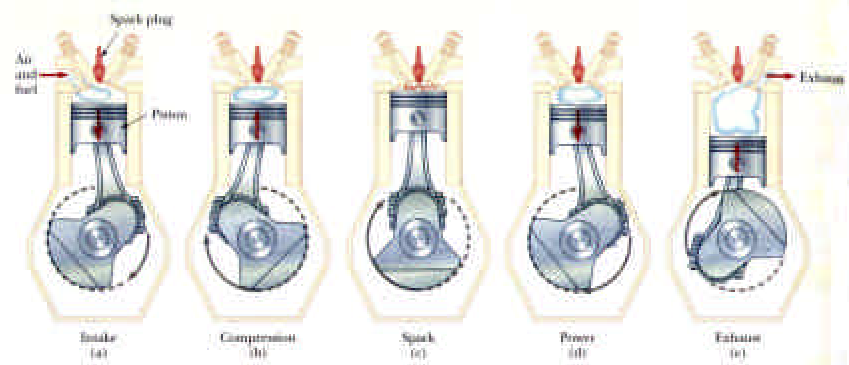


Ref.: Louis Schlapbach & Andreas Züttel, NATURE | VOL 414 | 15 NOVEMBER 2001 | pp. 353-358

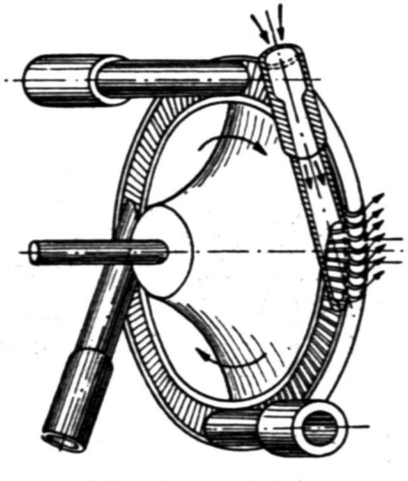
ENERGY CONVERSION DEVICES



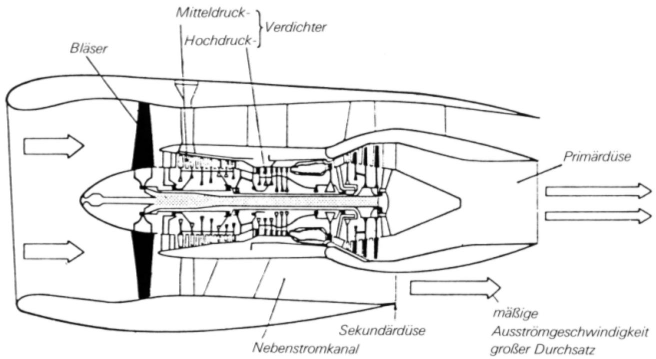
Steam engine



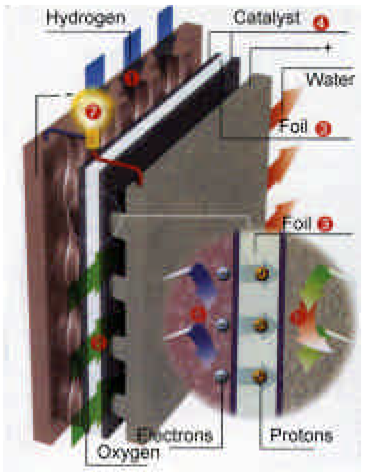
Internal combustion engine



Steam turbine



Combustion turbine



Fuel cell

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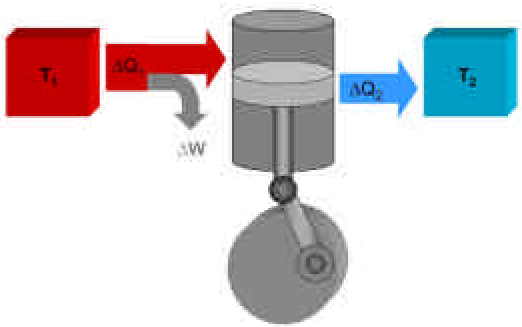
ENERGY CONVERSION ENGINES

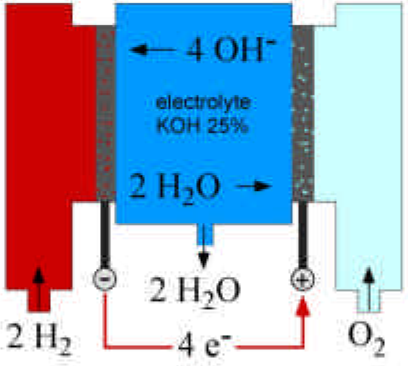
Réflexions sur la puissance motrice du feu (1824)



Sadi Carnot
(1796-1832)

$$\eta = \frac{\Delta W}{\Delta Q_h} = 1 - \frac{T_c}{T_h}$$

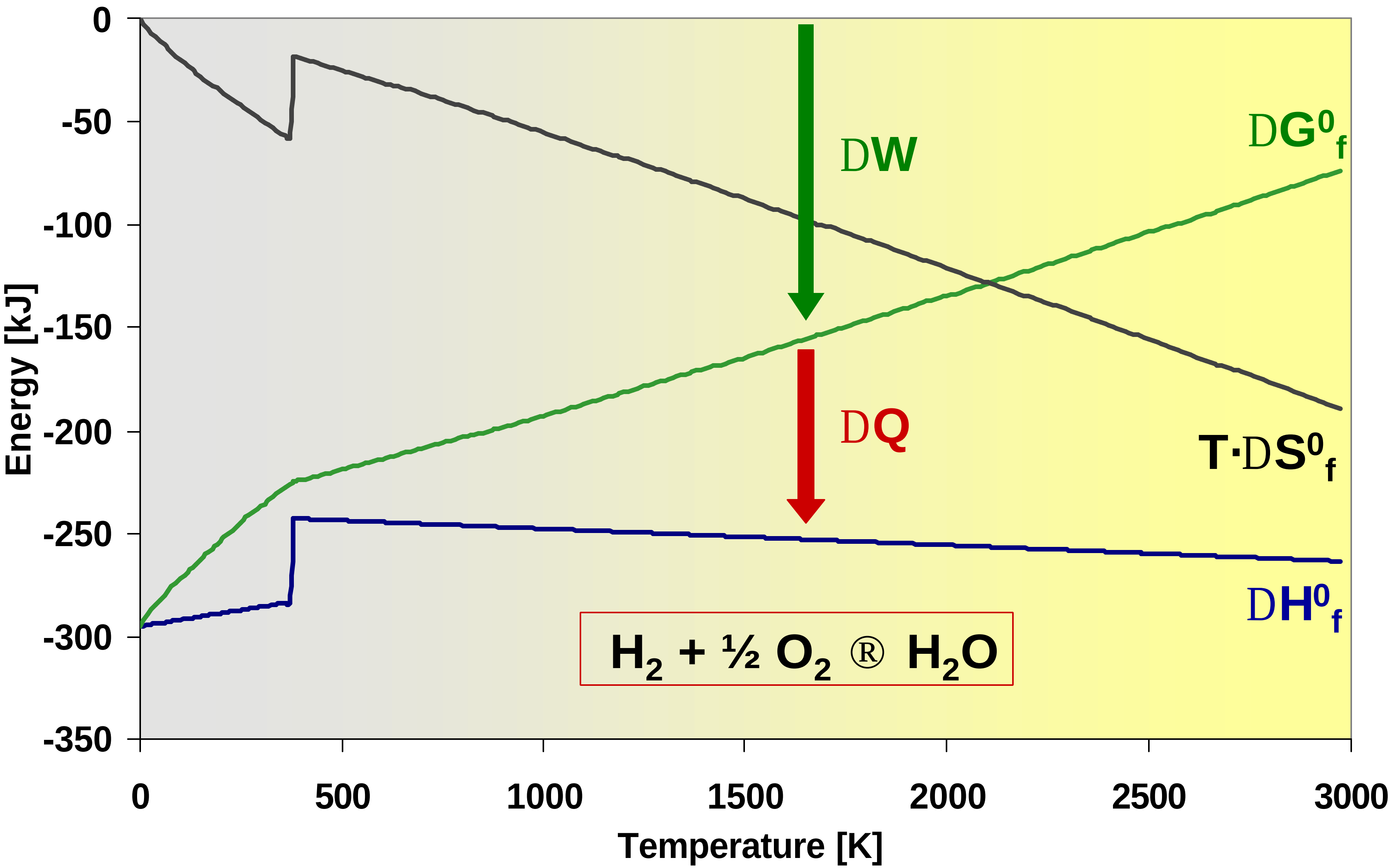
On the Correlation of Physical Forces (1846)



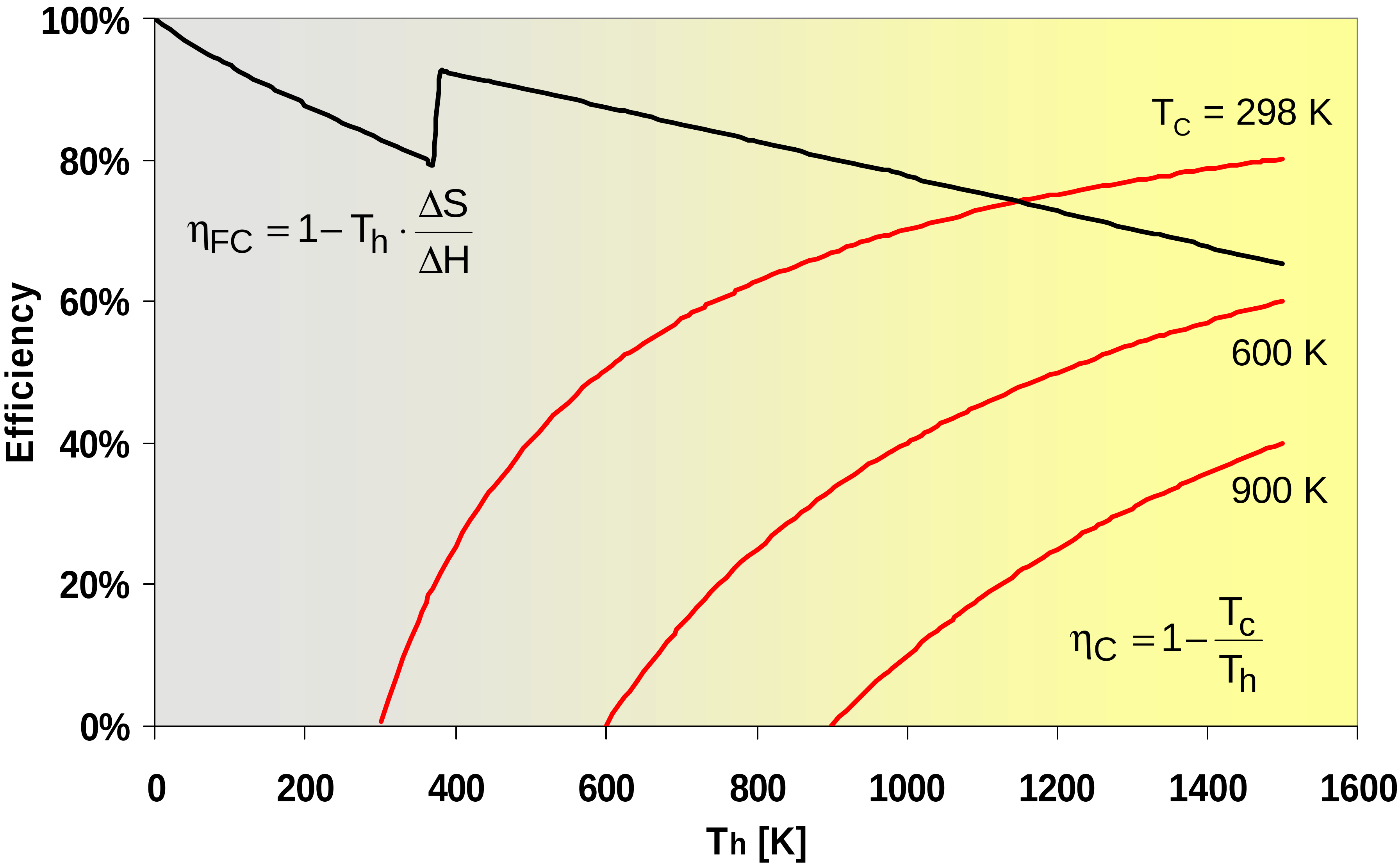
Sir William R. Grove
(1811–1896)

$$\eta = \frac{\Delta G}{\Delta H} = 1 - T_h \cdot \frac{\Delta S}{\Delta H}$$

WATER FORMATION



EFFICIENCY


100%
80%
60%
40%
20%
0%
Efficiency
0
200
400
600
800
1000
1200
1400
1600
Th [K]
$\eta_{FC} = 1 - T_h \cdot \frac{\Delta S}{\Delta H}$
T_C = 298 K
600 K
900 K
$\eta_C = 1 - \frac{T_c}{T_h}$

LZ 129 "HINDENBURG"

New York / Lakehurst, May 6th 1937, 6 pm

Accident:
While the airship was landing she has got on fire about 80 meters above ground level and crashed.
Fatalities:
13 of 36 passengers,
22 of 60 crew members
1 member of 228 ground staff holding the ship.

AF 4590 CONCORDE

Paris / July 25th 2000, 4:44 pm

Accident:
While the jet was taking off flames were noticed at the rear side of the left side wing.
All on board were killed:
9 crew, 100 passengers
4 people were killed on the ground.
5 injured on the ground, one seriously

HYDROGEN FOR MOBILITY

Hindenburg (1937)

Austin A40 (1966)

Tupolev 155 (1988)

Space Shuttle (1981-)

Saturn (1963-)

Necar 1 (1994)

NuBus, 250kW (2002)

BMW (1978-)

Necar 4 (2002)

SAM (2005)

DEMONSTRATION PROJECTS

BFE OFEN UFE SFOE

BFE OFEN UFE SFOE

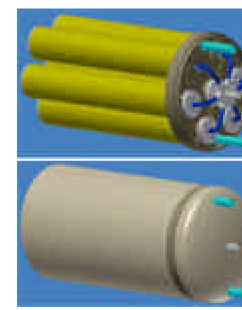
IESE

UNIVERSITAS FRIBURGENSIS

BFE OFEN UFE SFOE

Berner Fachhochschule

Hochschule für Technik und Informatik HTI



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PAUL SCHERRER INSTITUT

PSI

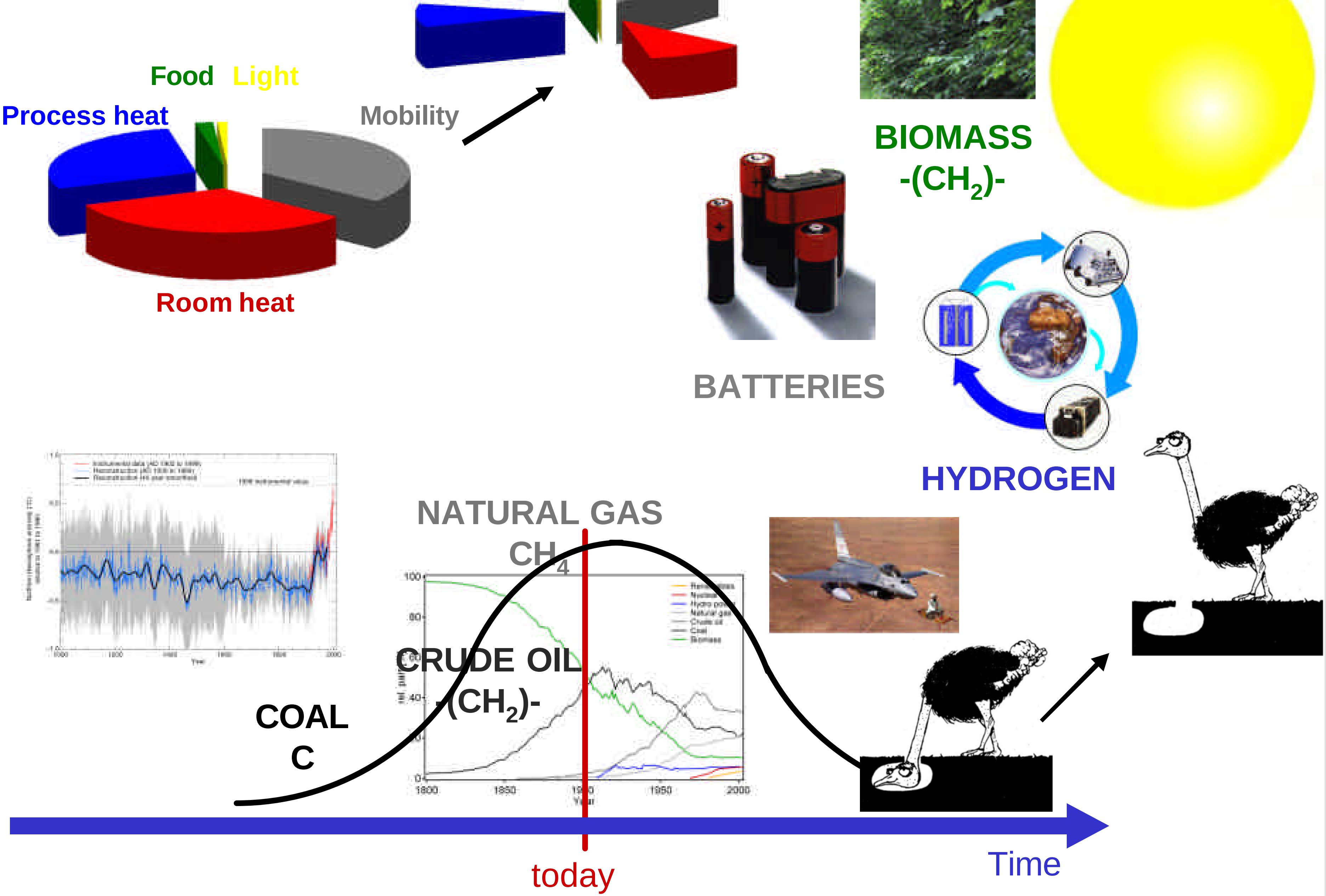
ETH

Eidgenössische Technische Hochschule Zürich

Swiss Federal Institute of Technology Zurich

BFE OFEN UFE SFOE

CONCLUSION



Andreas Züttel, IfRES (2005)

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Vrije Universitet Amsterdam, Faculty of Sciences
Condensed Matter Physics
URL: http://www.nat.vu.nl/CondMat/

HYDROPOLE
Swiss Hydrogen Association
URL: http://www.hydropole.ch