Sustainable Hydrogen and Electrical Energy Storage
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F.M. Mulder & M. Wagemaker

Hydrogen and Electrical Energy Storage part of Sustainable Energy Technology

MSc Program within 3TU

Fokko Mulder,
Marnix Wagemaker
TNW, R3
Fundamental Aspects of Materials and Energy

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Sustainable Hydrogen and Electrical Energy Storage

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2011

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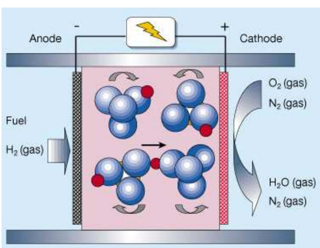

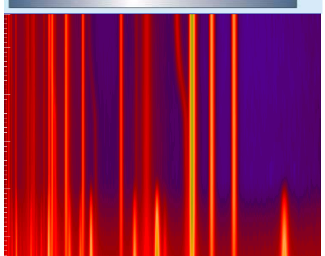

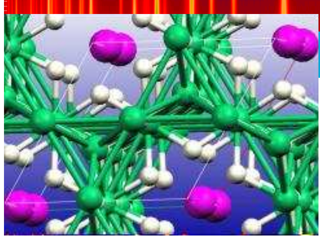

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Next to this material we use chapters of

- Hydrogen fuel: production, transport and storage
R.B. Gupta Editor
(available from library in pdf’s)

- Advanced Batteries, R.A. Huggins
(available from library in pdf’s)

- Research papers as background reading material

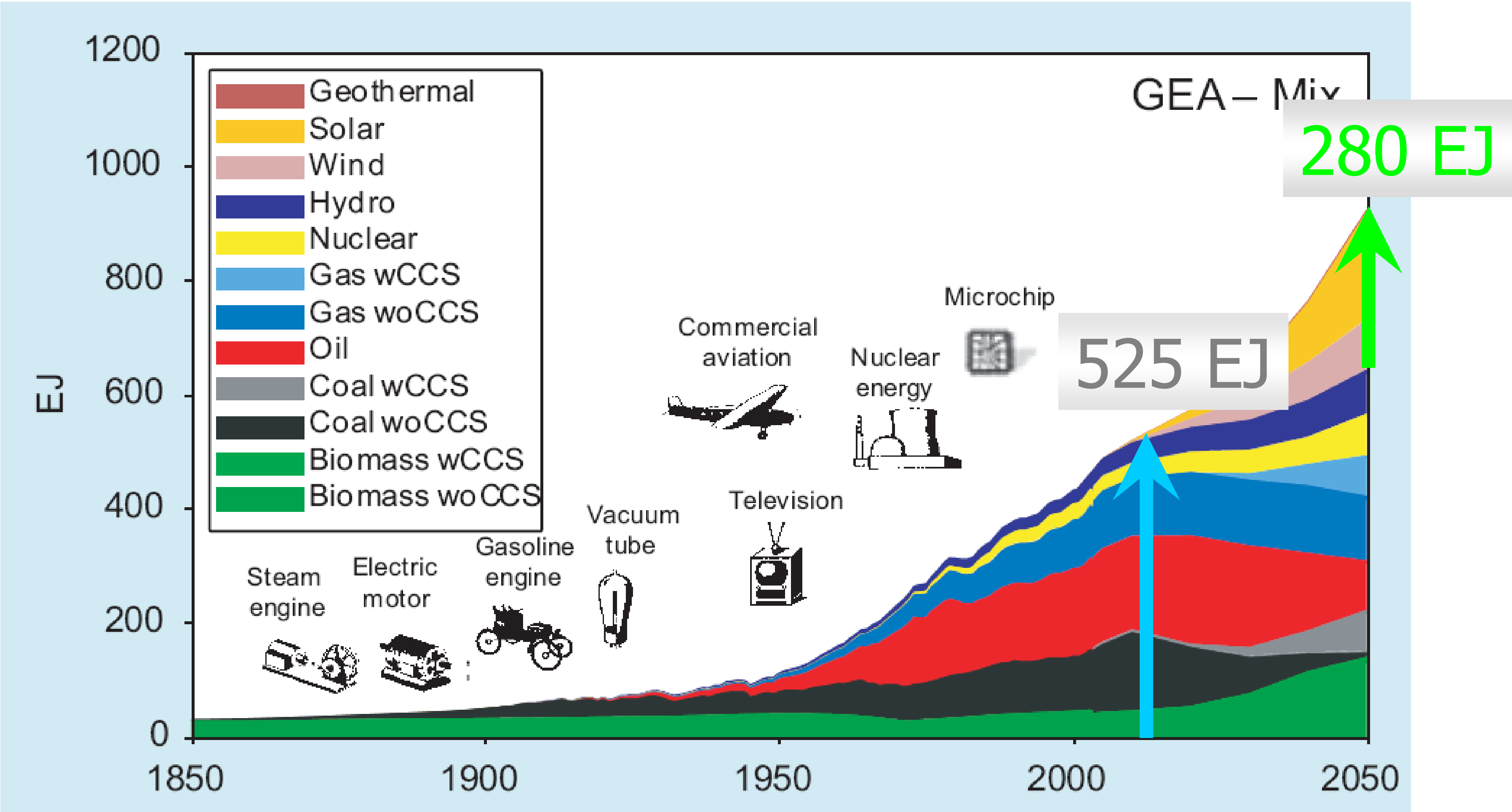
This field is under construction!

Why hydrogen and batteries for energy storage purposes?

Because we rely now on fossil fuel stores,
while renewable energy is not automatically stored.

Global Energy Assessment 2012

1EJ=10^{18}J



http://www.iiasa.ac.at/

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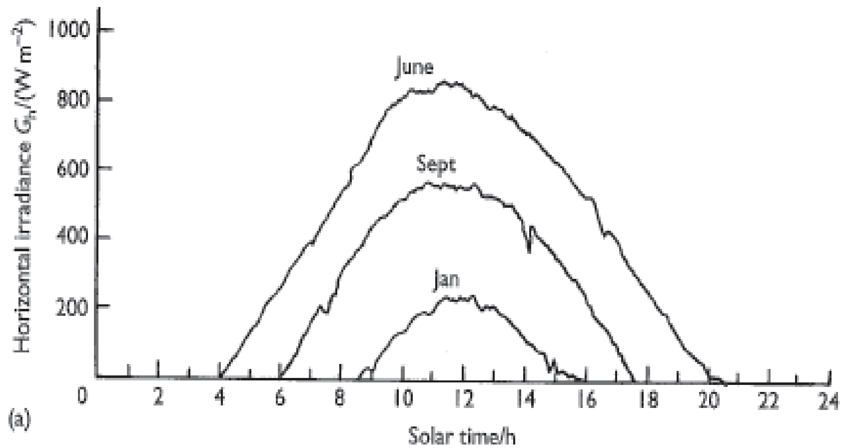
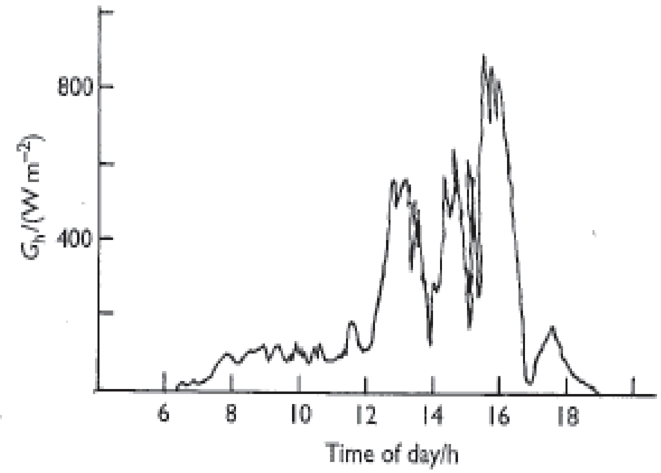
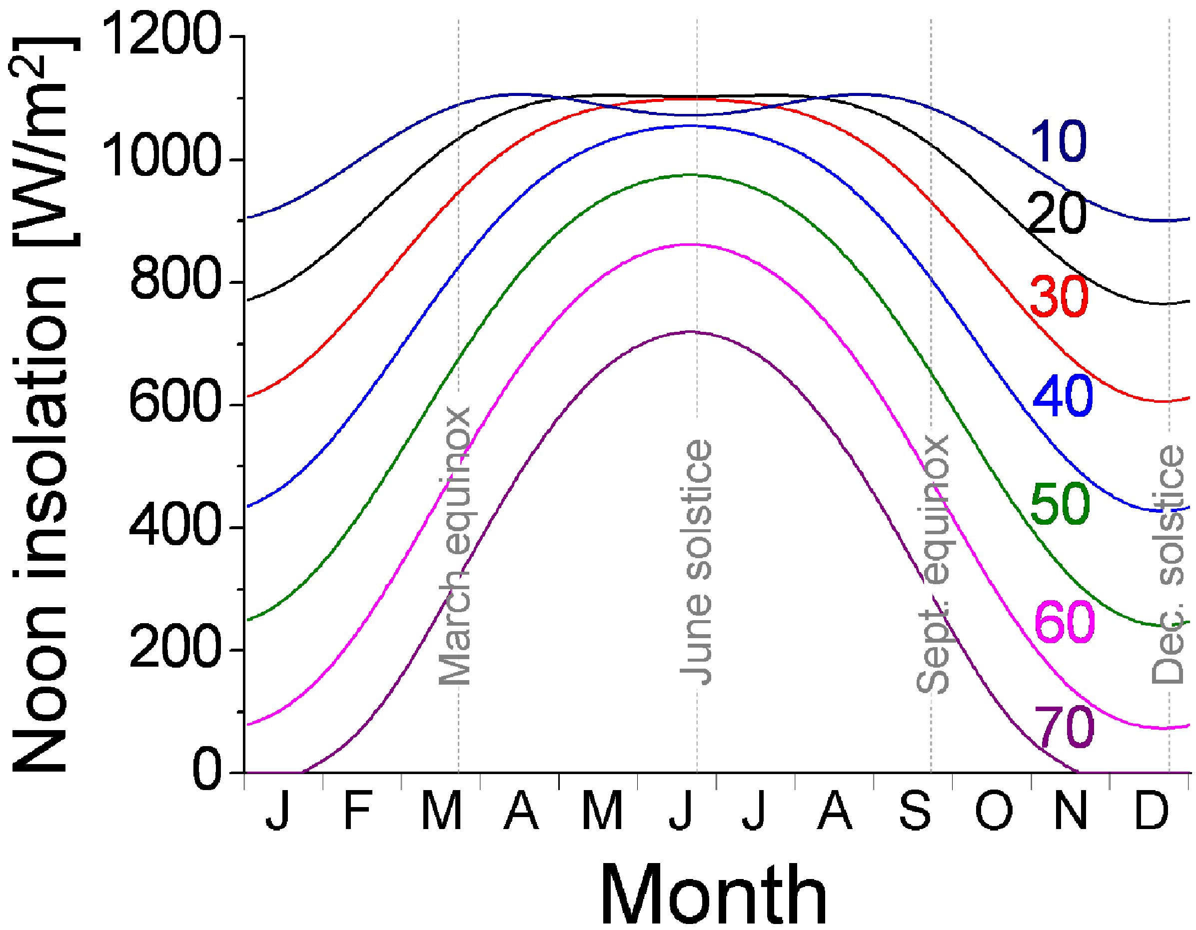
Solar power: largest resource of renewable energy



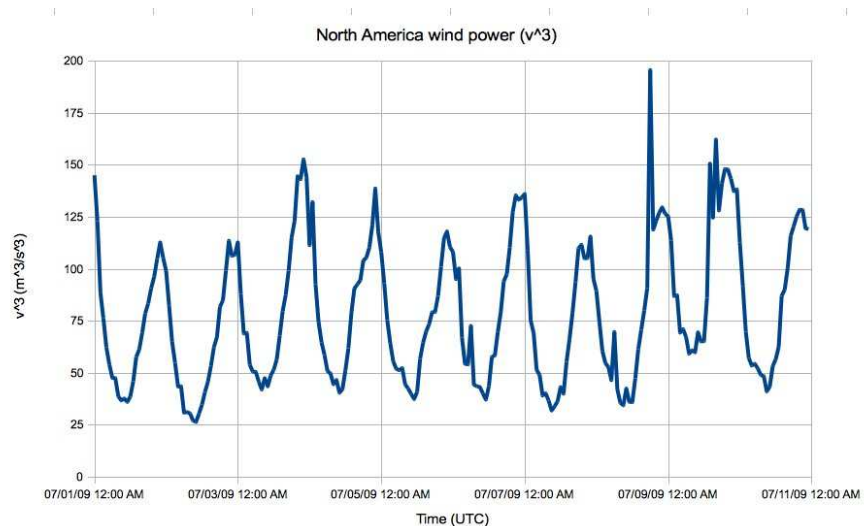


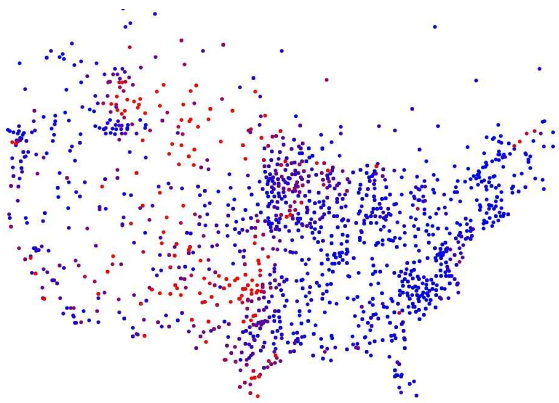
Factor ~ 6 between solar light in summer and winter (England)



Peak insolations at the different northern latitudes indicated

Large area still shows large wind power fluctuations





Windpower fluctuations (left) estimated from measured windspeed velocity data on METAR sites (right) in the US. On such integration scale highs occur during afternoon, lows during morning. Efficient electricity storage on the scale of hours and up to a day is required to make best use of the electricity produced by wind energy. The same applies to solar energy.

Wind and solar power are apparently shifted about 4 hours in time, so their highs and lows compensate only partly. Clearly the wind is also driven by the sun…

utc = time in Greenwich (~ 6h before central US)

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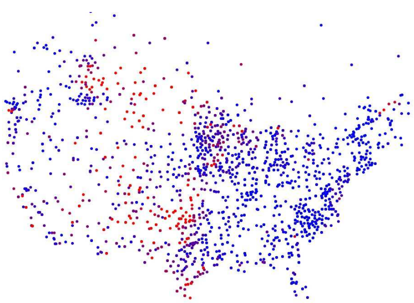
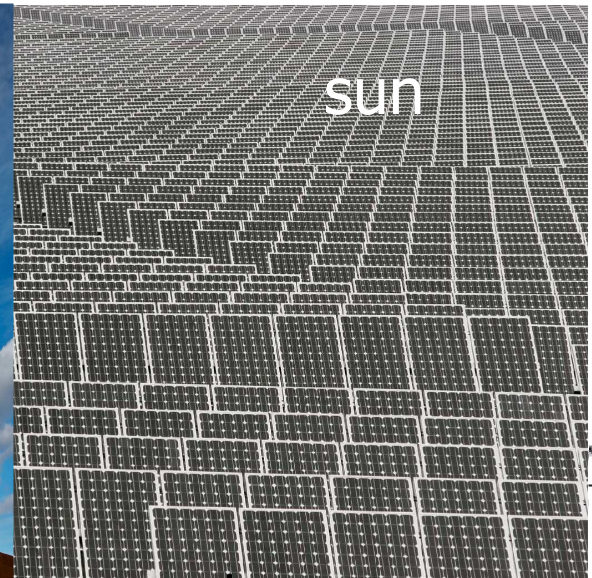
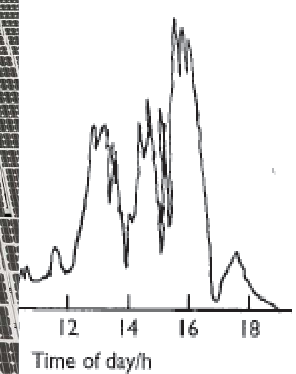
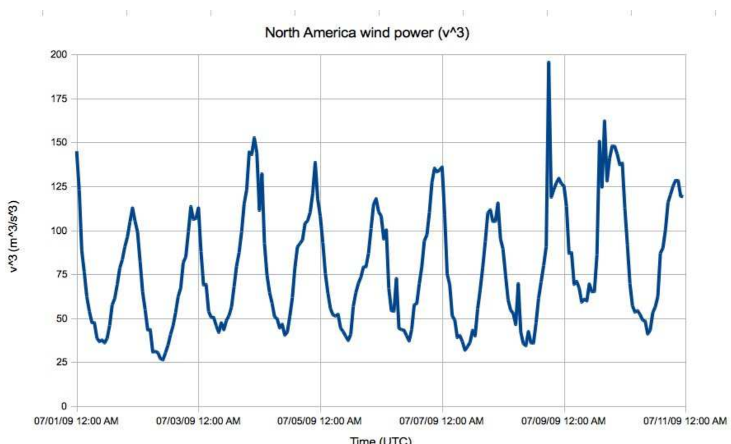
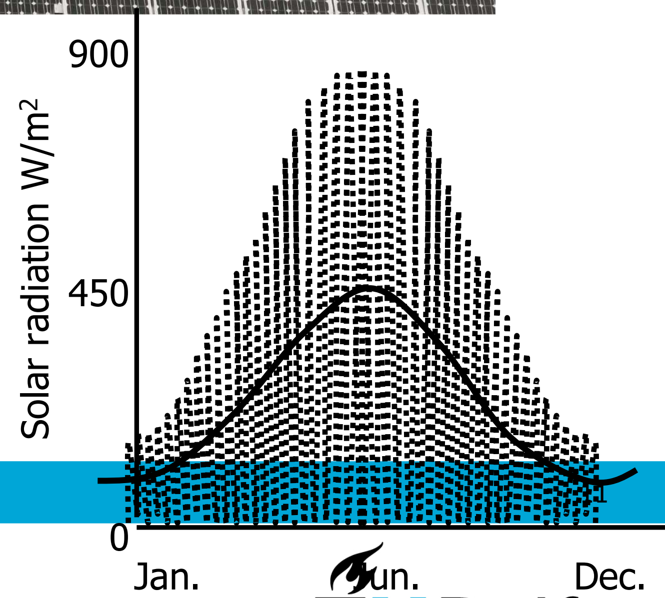
Renewable energies deliver systematically varying electricity











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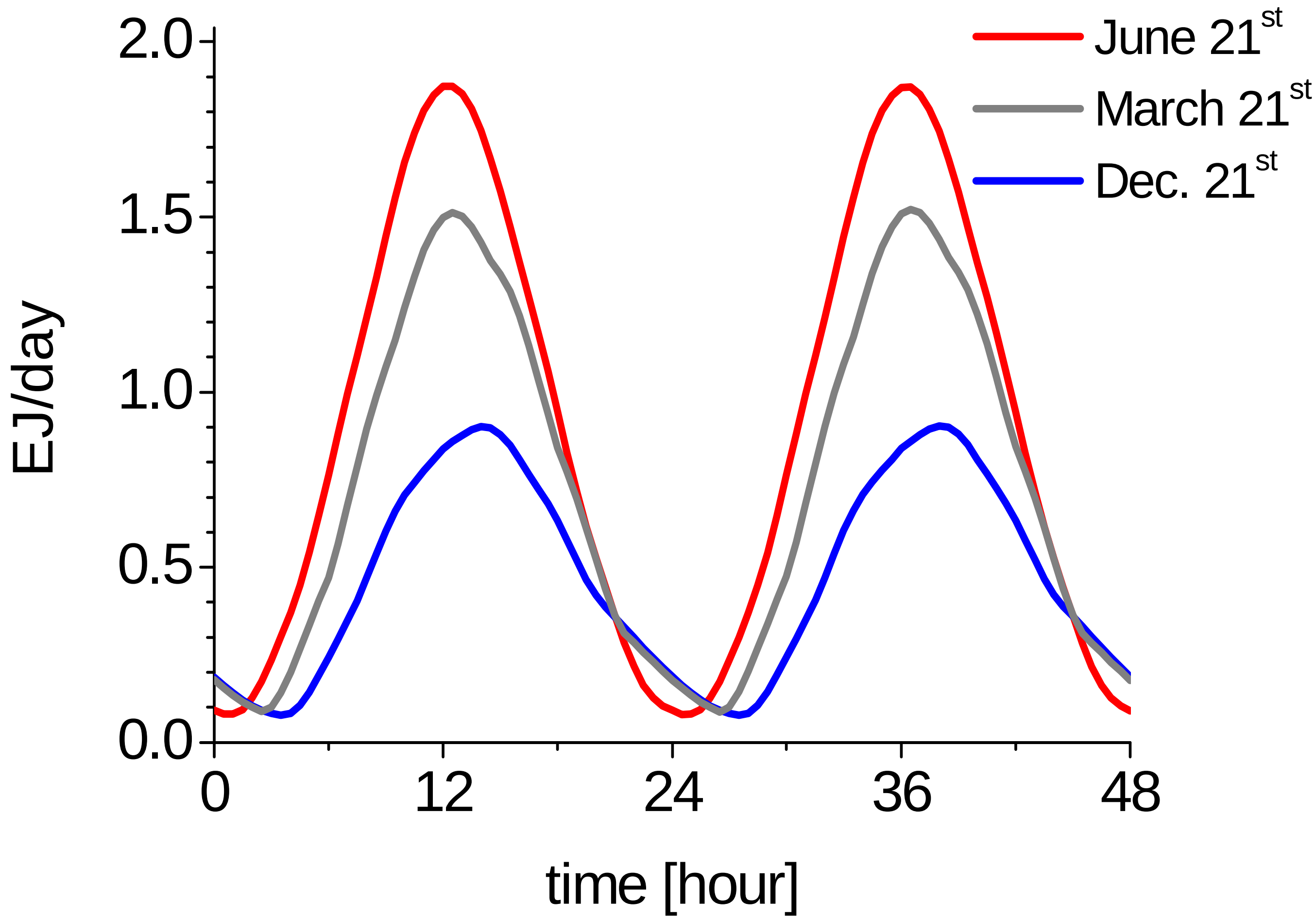
Example of sum of sun + wind by ~2050



Compare that to 900EJ/365d= 2.5EJ/day average use! (GEA prediction)

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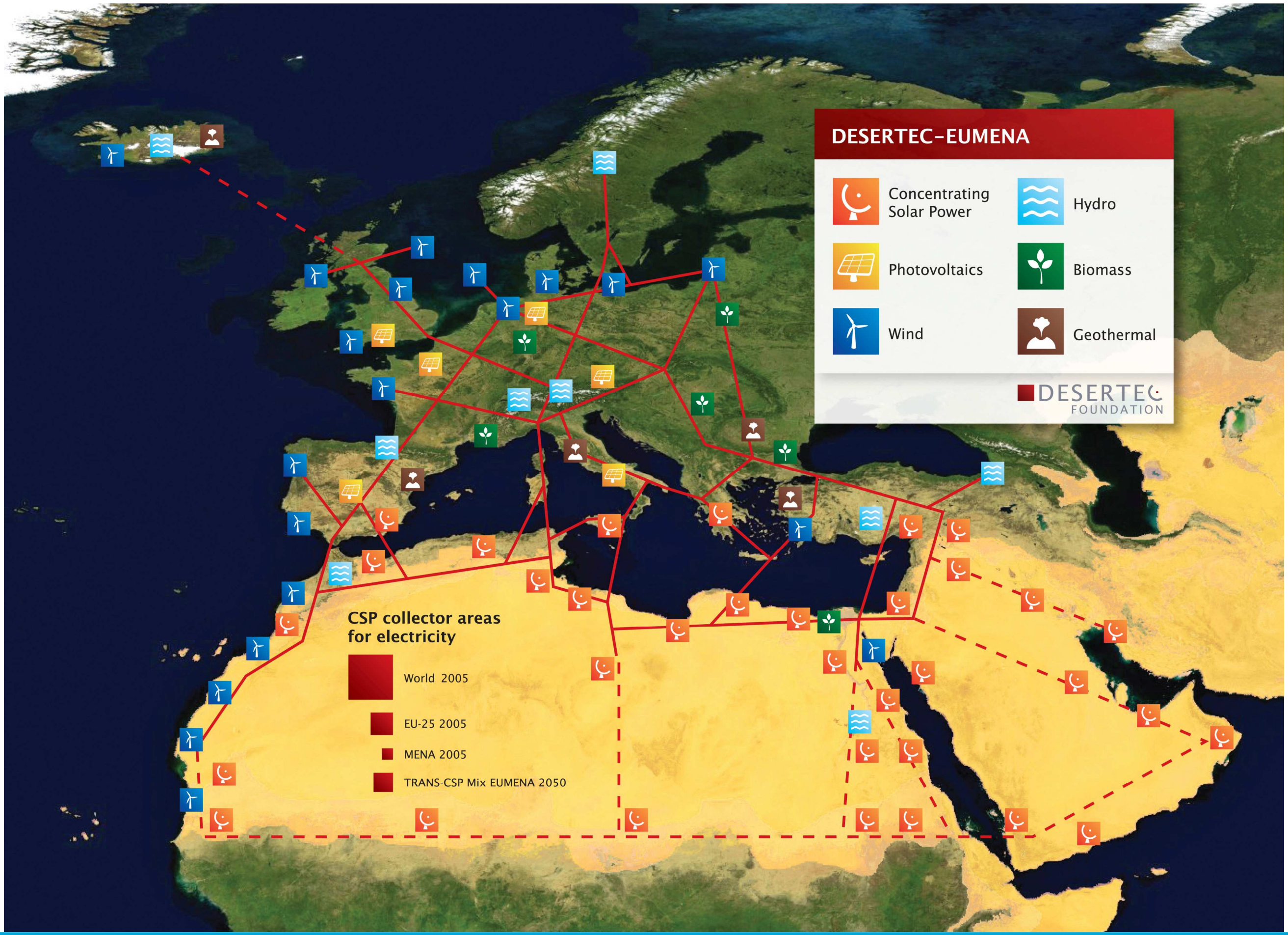
The largest connected grid of renewable electricity sources will show systematic variation. The sun drives it all.



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World wide smart grid?

- €ostly
- Long distance trans global electricity transport: losses

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What direction should the grid be extended to:

- Cancel day-night variation?

East-West

- Cancel summer-winter variation?

North-South

How far should the grid reach?

20000 – 30000 km

At 3% loss per 1000 km, how much would you loose?

$1 - 0.97^{20 \text{ or } 30} = 46\% \text{ or } 60\%$

How much energy should be transported through such ‘world grid’?

Good question!

Peak power (winter on northern hemisphere) maybe

(270EJ / 365 day) x 4 = 34 TW (?!)

Too much to handle

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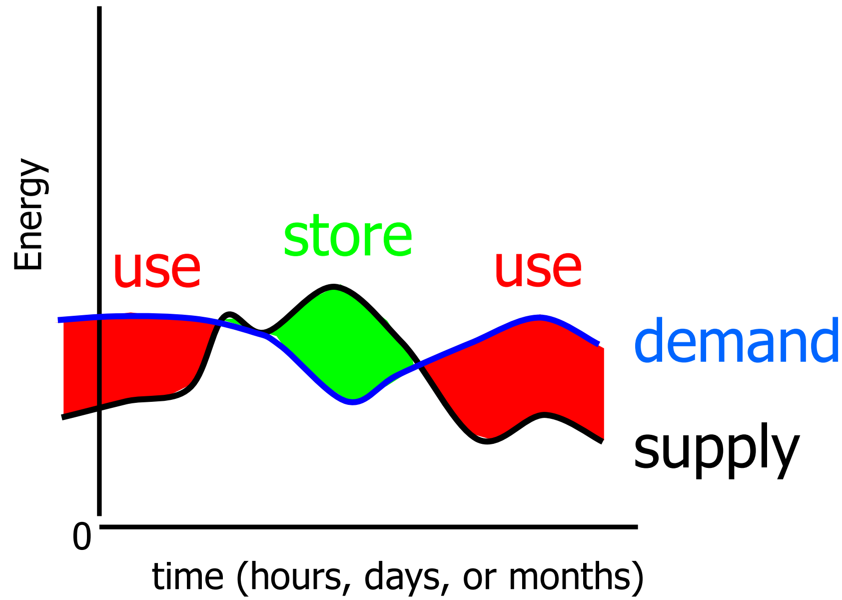
Energy storage and conversion



For the Netherlands the use of energy is ~2550 GWh/day.
By 2020 ~1/3 of electricity may come from windpower.
In 30 years renewable energy production -and its fluctuations- will be on a 100-ds of GWh/day scale.

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Energy storage at which scale?

Netherlands use ~2550 GWh/day (primary energy).

Future: significant fraction from renewables?

This means every day 100-ds of GWh fluctuations

→ Energy storage at least on 100-ds of GWh / day scale

Per household

7 million households in NL
→ at least few times x 14 kWh storage per household
→ whole day: 25 x 14 kWh = 350 kWh per household
→ Seasonal storage??? **(EU-law strategic reserve: 91 days)**

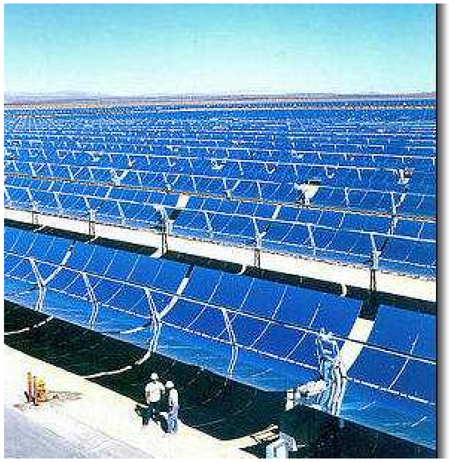
Energy storage with hydropower

Capacity: 20GWh $\rightarrow$ *~ 100 units for 1 day energy use*

Cost: 2.5 GEu.

Heat storage

- High T: In combination with concentrated solar power (CSP)
- Low T:
  - Put summer heat in depots or in water layers below the ground
  - Use heat in winter and put winter cold in the stores
  - ‘Up to 90% reduction of natural gas use in greenhouses’



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Energy storage for mobility

Lithium ion battery for electric car:
Average car drives 40 km / day, which would cost ~ 4 kWh / day.

4kWh x 7.3M cars = 29.2 GWh / day (NL 2006)
(compared to 4.3 GWh / day for the railways)

→ This is just a small fraction of the energy use in NL

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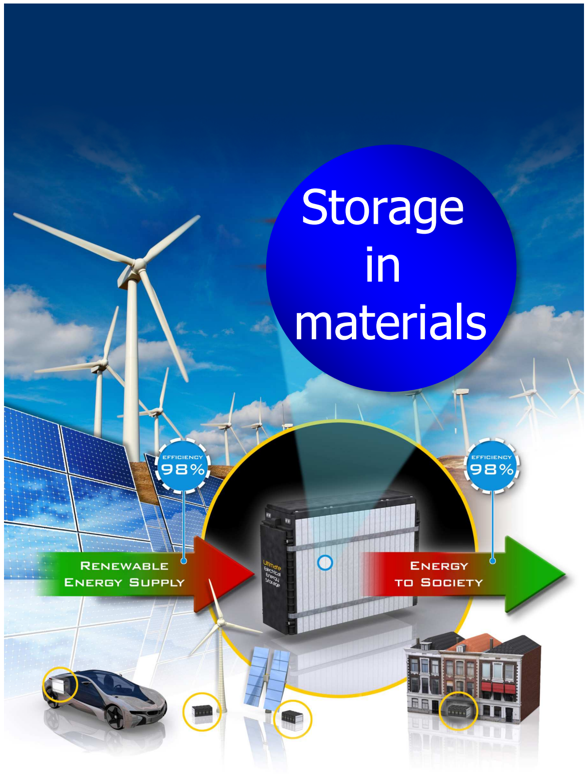
Potential contribution of electric transport to energy storage

Dutch electricity production: 175 GWh per day so 30 GWh is a substantial amount of energy. One needs 7300000 all-electric cars with their batteries to store this amount.

On world scale there is enough Li to produce a 200kg Li battery for 6 billion people in known reserves. There will be much more.

However, to store of the order of 100-ds or maybe 1000 GWh in electricity in batteries will require even larger amounts of batteries (remember: Dutch use ~ 2550 GWh for only 1 day).

Storage of energy on large scales is essential to enable large scale application of solar and wind power



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Why hydrogen as energy carrier and storage medium?

- Fossil fuels are running out: Oil: ~**32 years**

  Gas: ~**72 years**

  Coal: ~**252 years**

numbers from EIA, Energy Information Administration, US Government, for 'easy recoverable' fuels

- Hydrogen is a clean energy carrier
- Potentially no CO_2 emission, less greenhouse gasses
- Independence from other (fossil) fuel suppliers

- It can be produced everywhere where there is water and energy, no carbon needed. So it is made of **abundant** elements.

- Green alternatives like ethanol or methanol require C which is only at ~380 ppm level present in air in the form of CO_2, and requires agricultures to collect it (or fossil fuels).

- It can be used directly in engines that are slightly modified

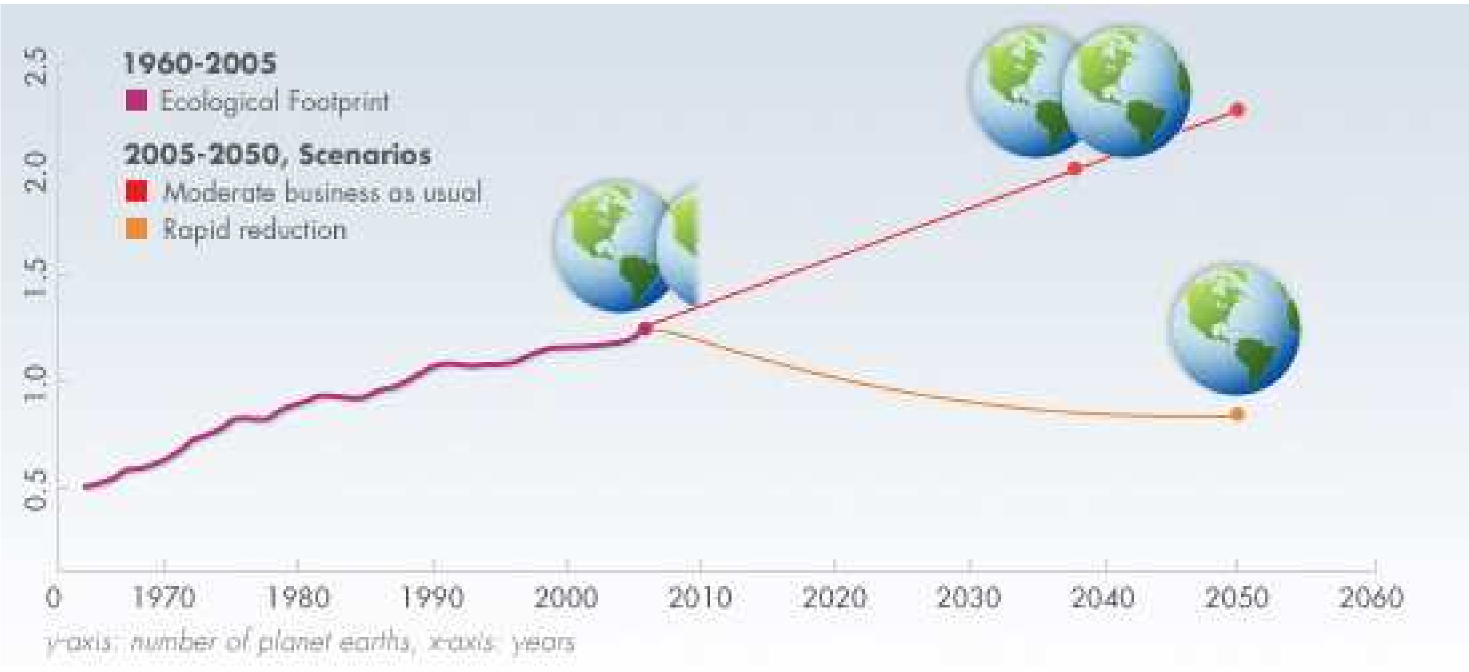
- In future more efficient solutions to use H_2 may be realized on a commercial scale like fuel cells: potential for improvements

- It is a gas, so it can be transported cheaply through pipelines

- when spilled it rapidly dissipates under good ventilation

Hydrogen as clean energy carrier could help reduce the impact of humanity on the environment.

Ecological footprint: description of the burden of humanity on the ecosystem expressed in the number of earth's required to carry that burden. Currently ~1.3 earth is required to support humanity.



From www.footprintnetwork.org

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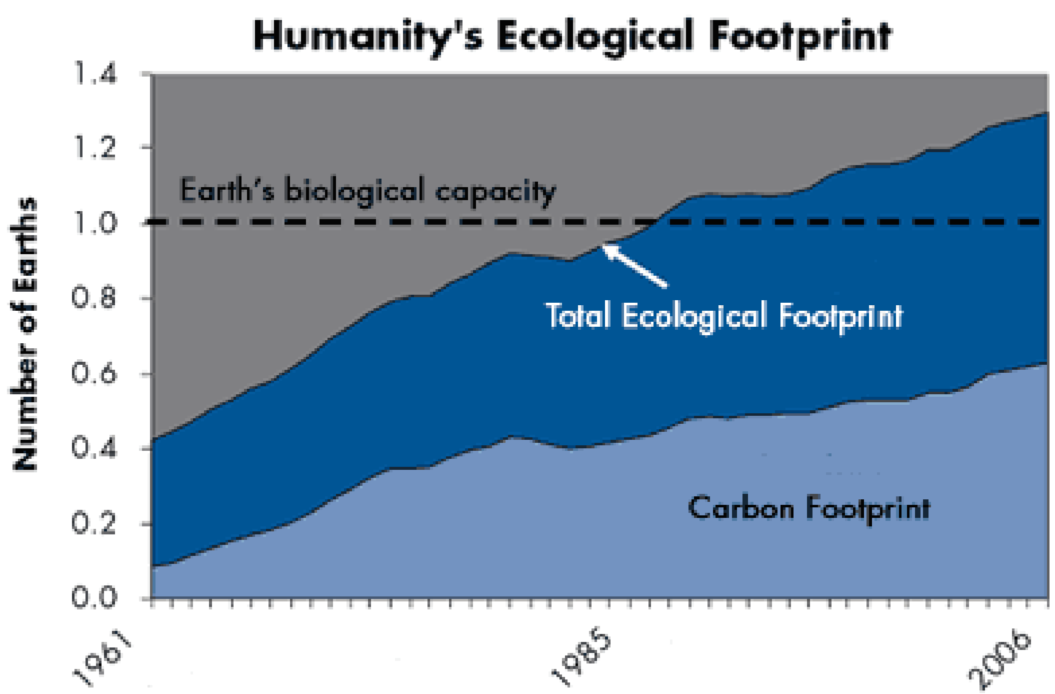
Carbon footprint: the amount of forest required to sequester all CO_2 emitted divided by available forest on earth.
(note sequestration in wood is mostly only temporary)
Reducing CO_2 emission by implementing a clean hydrogen economy will reduce carbon footprint.



Why is there *no* large scale implementation of hydrogen yet?

- hydrogen has to be produced

- costs are too high per kWh, it is not coming out of the ground for free

- it is a gas and has to be stored in some efficient way: space, cost and weight requirements of storage

- in the transport sector factors like storage, safety and efficient use by fuel cells are not economical yet.

- needs large modifications of energy distribution systems. H_2 can cause embrittlement of metal pipe lines

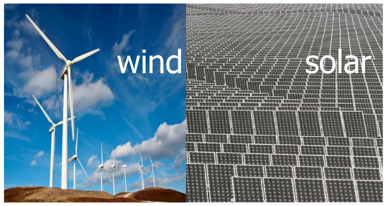
- safety aspect: can burn in air in low concentrations

A potential carbon free energy economy?
(a ‘private working model’)

- Use renewable electricity if possible directly from the smart grid
- If not possible: have short time (< 1 day) efficient storage in the form of batteries available
- There should be long term solar power overproduction during summer to make up for lower production in winter. Such overproduction cannot be stored in batteries, so convert this to hydrogen (with lower efficiency).

Largest scale storage in central depots? Use only abundant materials:

- Combine hydrogen and nitrogen (70% in air) into **liquid ammonia**. This is a well known industrial process. Store this as large scale central storage.
- When generating H_2 from ammonia use NH_3 binding salts like $MgCl_2$ to filter out poisonous NH_3 traces from gas streams, and feed H_2 to central power plants on the grid. Exposure limit in air: 50 ppm.
- Normal consumers may use materials like catalyzed MgH_2 when storing H_2 because they probably cannot work with poisonous NH_3 (safety).

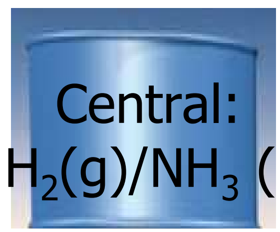


Future Storage Capacity [% daily energy use]

Smart Grid

	direct use	0%
η ~ 98%	batteries	<100%
		<10%
η ~ 60%	H_2	>9100%

350kWh/household



Central:
$H_2(g)/NH_3$ (l)

Users:
MgH_2

Solar heat and winter cold via heat storage x %

History and general properties of hydrogen

Read also CH1 of Gupta book

Discovery of HYDROGEN

- Hydrogen gas, H_2, was first artificially produced and formally described by T. Von Hohenheim (also known as Paracelsus, 1493–1541) via the mixing of metals with strong acids. He was unaware that the flammable gas produced by this chemical reaction was a new chemical element.

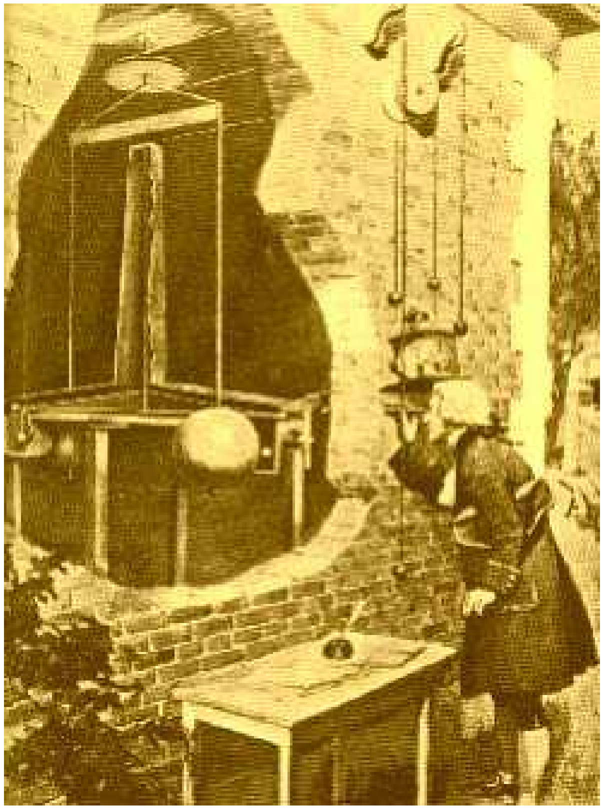
- In 1671, Robert Boyle rediscovered and described the reaction between iron filings and dilute acids, which results in the production of hydrogen gas.

- In 1766 Cavendish described the reaction of Hg and acids and described some properties of hydrogen. He is considered as discoverer of the element.

- In 1781 Cavendish burnt his „burning air“ (oxygen) with this new „fire air“ and obtained nothing but water.

- Hydrogen, Latin: 'hydrogenium', is from Ancient Greek ὕδωρ (hydro): "water" and (genes): "forming". This name is given by Lavoisier.

Cavendish



Cavendish is also known from 1st measuring the Gravitational constant using a torsion balance in 1798

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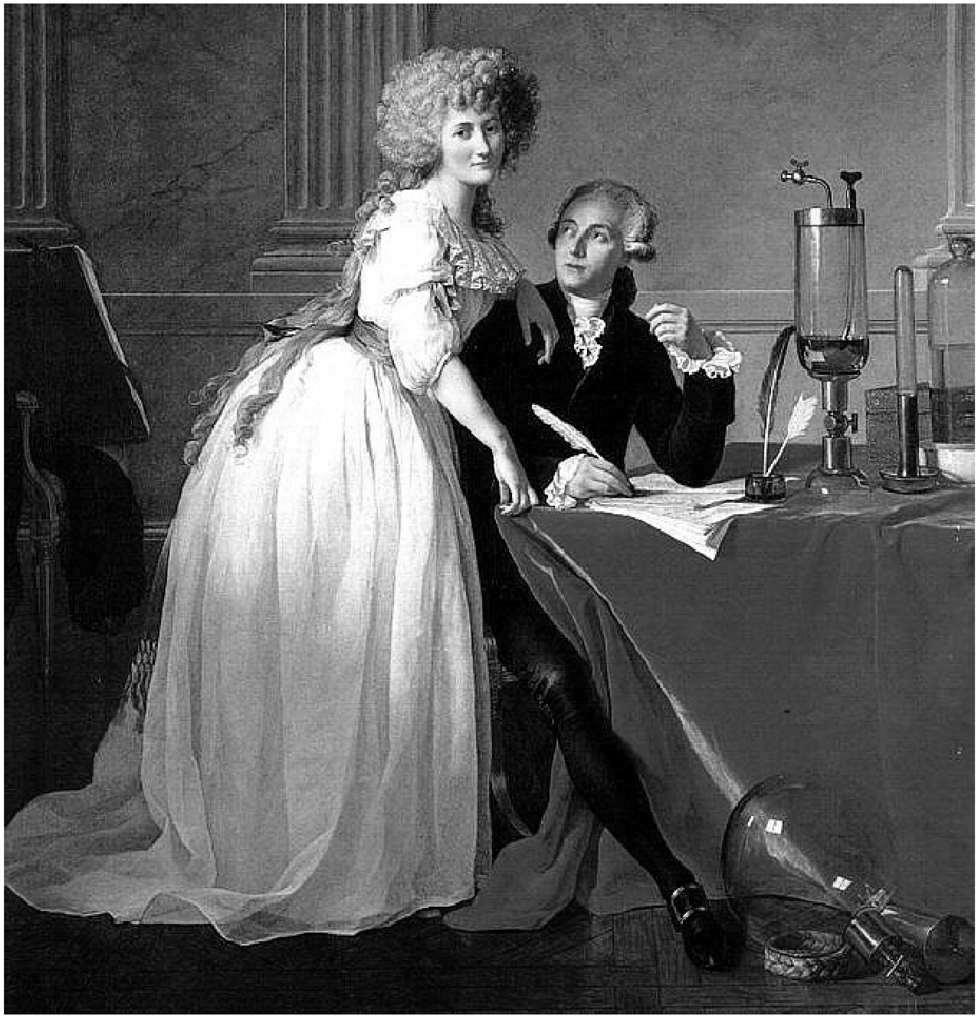
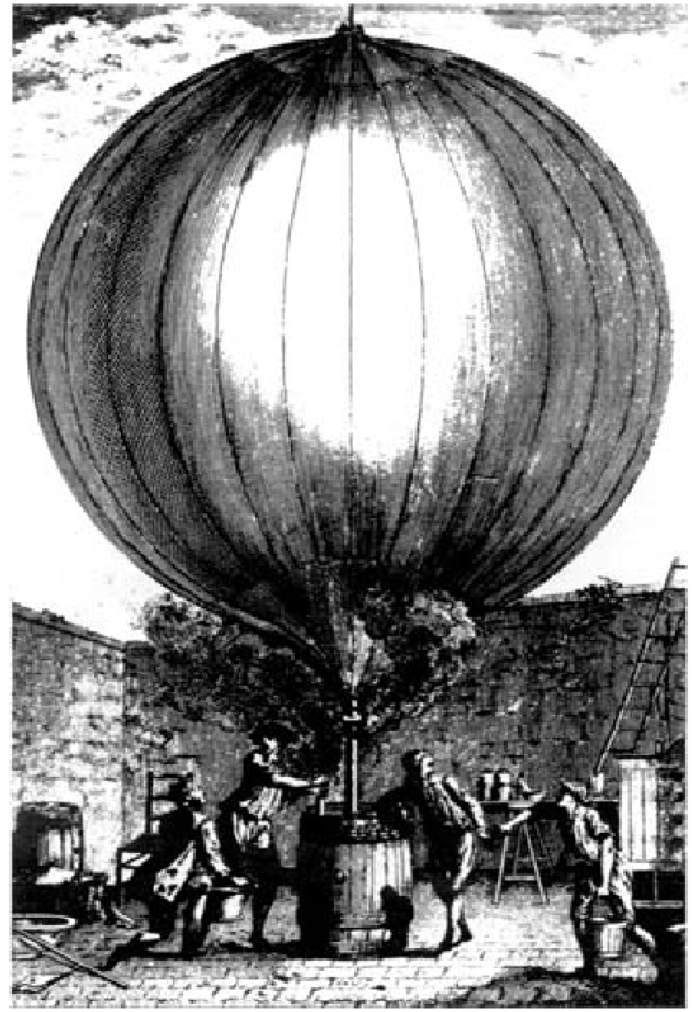


Antoine Laurent Lavoisier (1743 - 1794) with his wife and collaborator Marie Anne.



Alexandre Cesar Charles with his hydrogen filled balloon in 1783

Hydrogen for transport!

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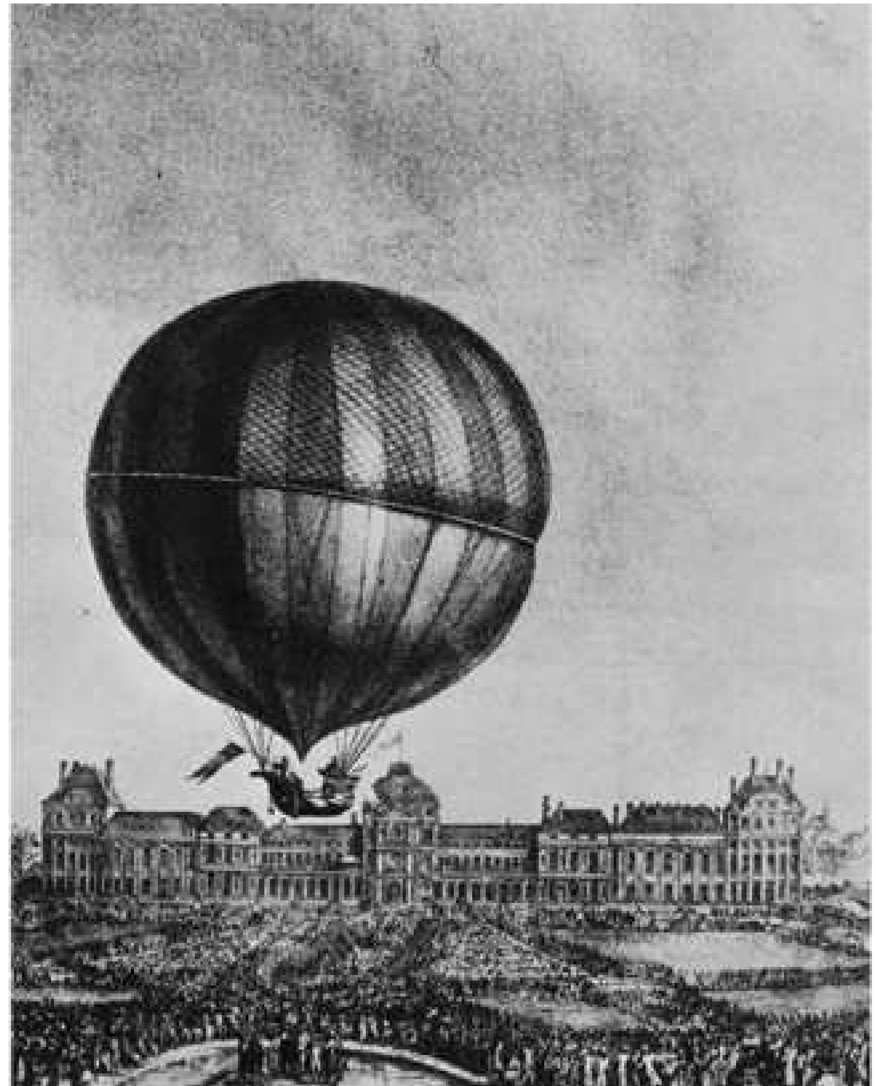
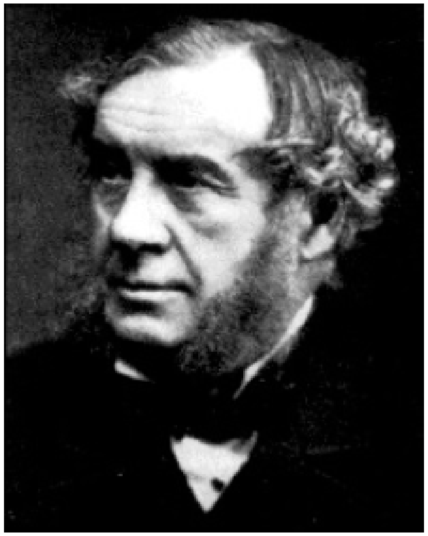
- On June 5, 1783 the Montgolfier brothers made their first successful flight with a balloon.

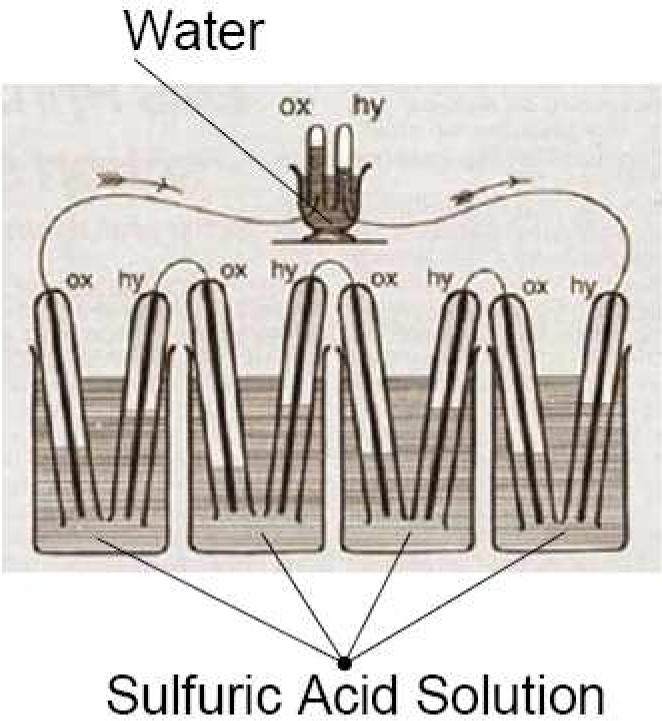


Alexandre Cesar Charles, a French scientist not knowing that the Montgolfier brothers had used hot air for their balloon, made a flight up to 3000 feet on August 28 of the same year with a balloon filled with hydrogen. The hydrogen necessary to fill his balloon was obtained by pouring sulphuric acid onto iron chips in a barrel placed below the balloon. After landing the balloon was destroyed by terrified peasants…

$$Fe\ (s) + H_2SO_4\ (aq) \rightarrow H_2(g) + FeSO_4\ (aq)$$

-1839: Sir William Grove constructed the first hydrogen fuel cell.





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- 1861: Germans Kirchhoff und Bunsen demonstrated the presence of hydrogen in the spectra of the Sun. Then it became evident that hydrogen was the most abundant element in the Solar System.
- 1954: Eduard Justi describes the use of hydrogen as energy carrier.
- 1969: Bockris et al. describe an ‘overall hydrogen energy concept’ (Int.J.Hydrogen Energy, **8**, 323-340 (1983)).
- 1970: Dr. Karl Kordesch builds hybrid fuel cell battery car.

Sharp looking car!

- Hydrogen is the lightest element of the Periodic System, but about 90 % of all atoms are hydrogen atoms. Together they account for about 75 % of the total mass known in the Universe.

- Hydrogen produced on Earth is able to escape the gravitational field. This is one explanation of the very low concentration of hydrogen gas in our atmosphere.

Physical properties

Appearance: colourless, odourless gas under standard conditions.
The stable form is di-hydrogen, H_2

Density of gas (0 °C, 101.325 kPa)	89.88 g/m^3
(air: 1200 g/m^3)	
Melting point:	14.01 K
Boiling point (1 Bar):	20.28 K
Liquid density (at 20 K):	70.8 kg/m^3
Triple point:	13.8033 K, 7.042 kPa
Critical point:	32.97 K, 1.293 MPa

Isotopes

^1H: 99.985%
^2H: 0.0115%
^3H: unstable (radioactive) with 12.32 yr half life. $^3H \rightarrow {}^3He + \beta^-$

H in Periodic system

H's formal oxidation states: +1, -1

H is placed in the group 1, but chemically it can also behave as a group 17 element

H^+F^-
↕
Li^+F^-

Li^+H^-
↕
Li^+F^-

Group / Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
** Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Historical use of hydrogen

- Balloons, zeppelins
- around 1800: mainly lighting and heating
- production of ammonia from N_2 and H_2

$N_2 + 3H_2 \rightarrow 2NH_3 + 92.4$ kJ/mol

@500 ^oC, 250Bar, Fe_2O_{3-x} catalyst

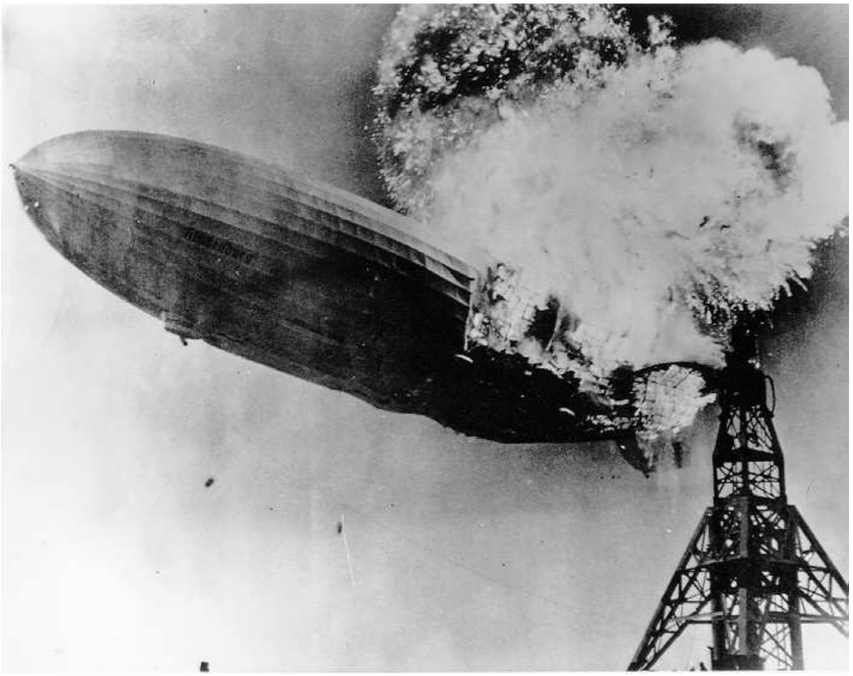
(Haber process 1909, Nobel prize 1918)

Ammonia used for : fertilizers, chemicals, explosives like NH_4NO_3 , plastics, fibres, pharmaceuticals, cleaning, …

Historical use of hydrogen

- saturation of unsaturated fat and oils in food industry
- production of methanol from $CO + 2H_2$
- production of HCl from $Cl_2 + H_2 \rightarrow 2HCl$
- reducing agent of metal ores
- shielding gas for welding electrodes
- electronics: production of semiconductors for IC's
- rocket fuel
- metal hydride batteries

Hydrogen as energy carrier

Hindenburg at Lakehurst 1936 and in flames in 1937

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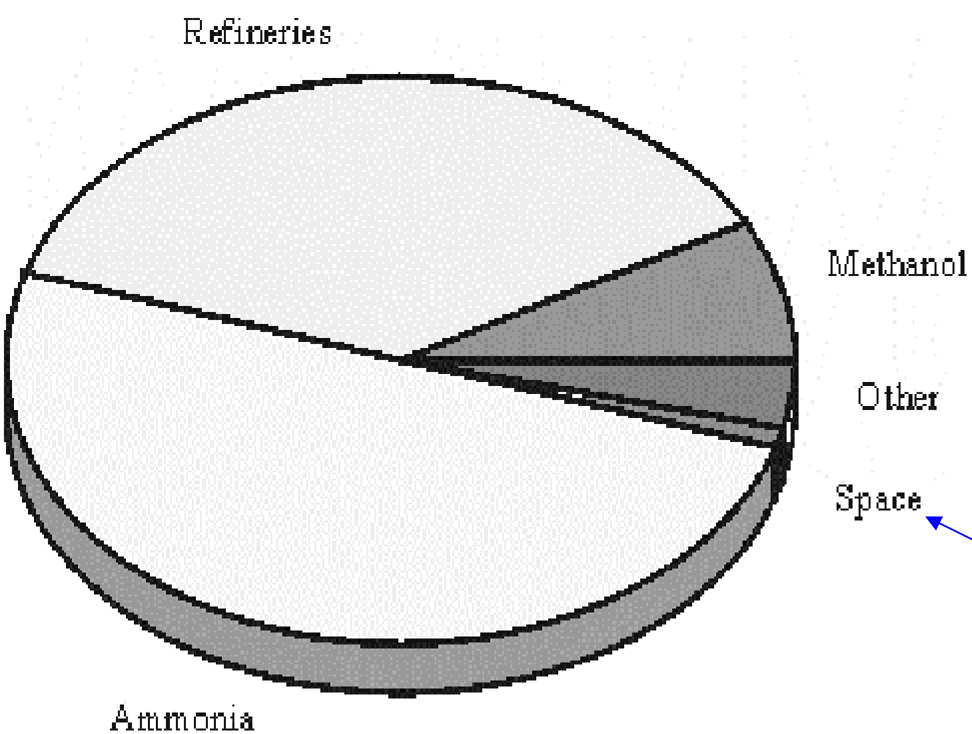
Current use of hydrogen

- mainly ammonia production
- oil refining
- methanol production
- all historical applications

• In oil refineries, hydrogen is used for upgrading the more viscous oil fractions to produce products such as gasoline and diesel and for removing contaminants such as sulphur.

• Demand for hydrogen in refineries is increasing dramatically as standards for fuels tighten in the US and Europe and as sulphur content is driven down.

Current use of hydrogen



World wide production:

45 million tonne/y

~ 6 EJ

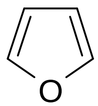
(1 EJ = 10^{18} Joules)

Pure hydrogen as energy carrier

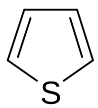
Source: http://www.ieagreen.org.uk/h2ch2.htm

Examples of hydrogen consumption in refineries

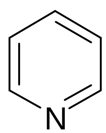
- Hydrotreating / hydroprocessing



$+ \ 4H_2 \rightarrow C_4H_{10} + H_2O$ *HDO, Hydro de-oxygenation*



$+ \ 4H_2 \rightarrow C_4H_{10} + H_2S$ *HDS, Hydro de-sulfurisation*



$+ \ 5H_2 \rightarrow C_5H_{12} + NH_3$ *HDN, Hydro de-nitrogenation*

In addition loss of hydrogen (can be upto 20% of consumption) *via*

- Hydrogenolysis (e.g., CH_4 formation)
- Hydrogen dissolution in oils,

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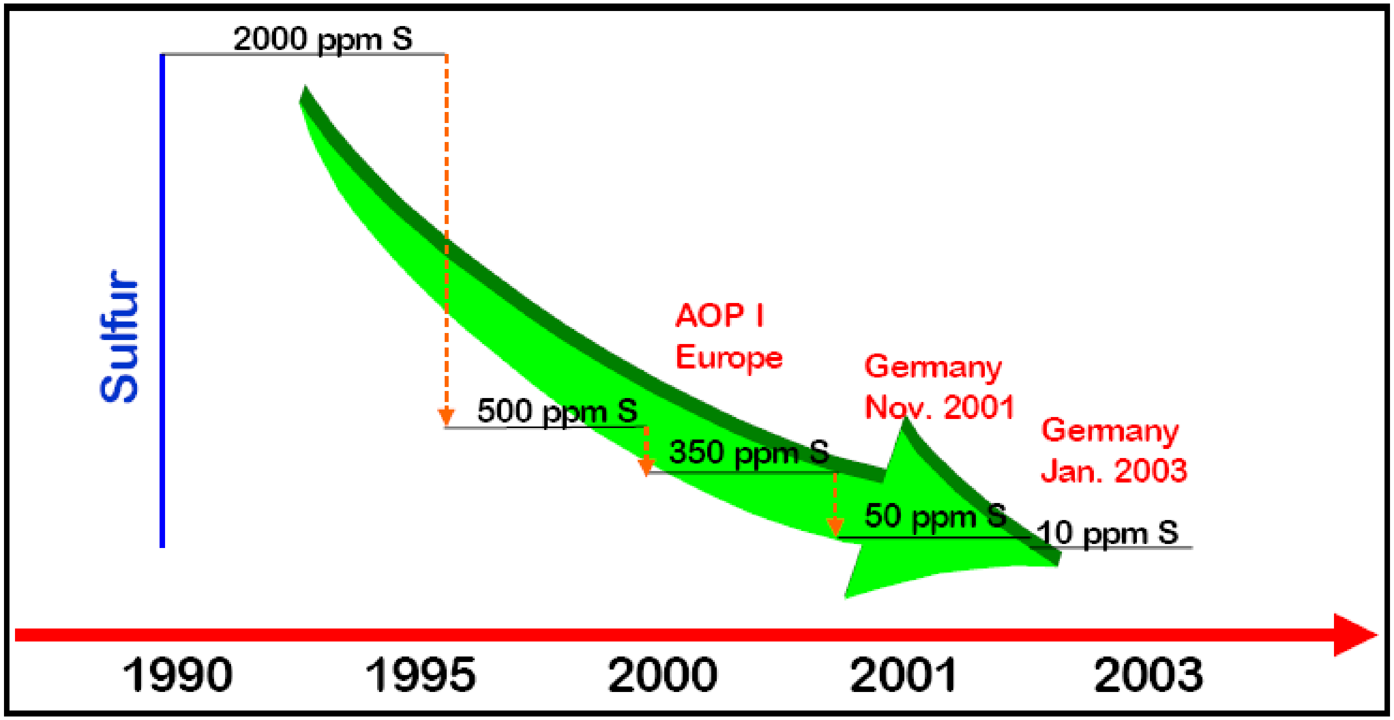
Sulfur specifications in diesel – EU

Increasing importance of hydro de-sulfurisation leads to increased hydrogen use



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Liquid fuels – EU quality requirements

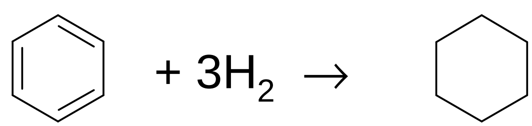
More increased hydrogen use due to regulations: dearomatisation

Gasoline	1996	2000	2005	2005-2010?
Sulfur	500 ppm	150 ppm	50 ppm	10-30 ppm
Benzene	5%	1%	1%	< 1%
Aromatics	not specified	42%	35%	< 30%
Olefins	not specified	18%	from 18% to 8%*	< 10%

Diesel	1996	2000	2005	2005-2010?
Sulfur	500 ppm	350 ppm	50 ppm	10-30 ppm
Cetane	49	51	from 51 to 58*	53 up to 55
Polyaromatics	not specified	11%	from 11% to 2%*	1%-2%
Specific gravity	860	845	from 845 to 820*	< 840
T95 max	370°C	370°C	340 to 360°C	< 340°C

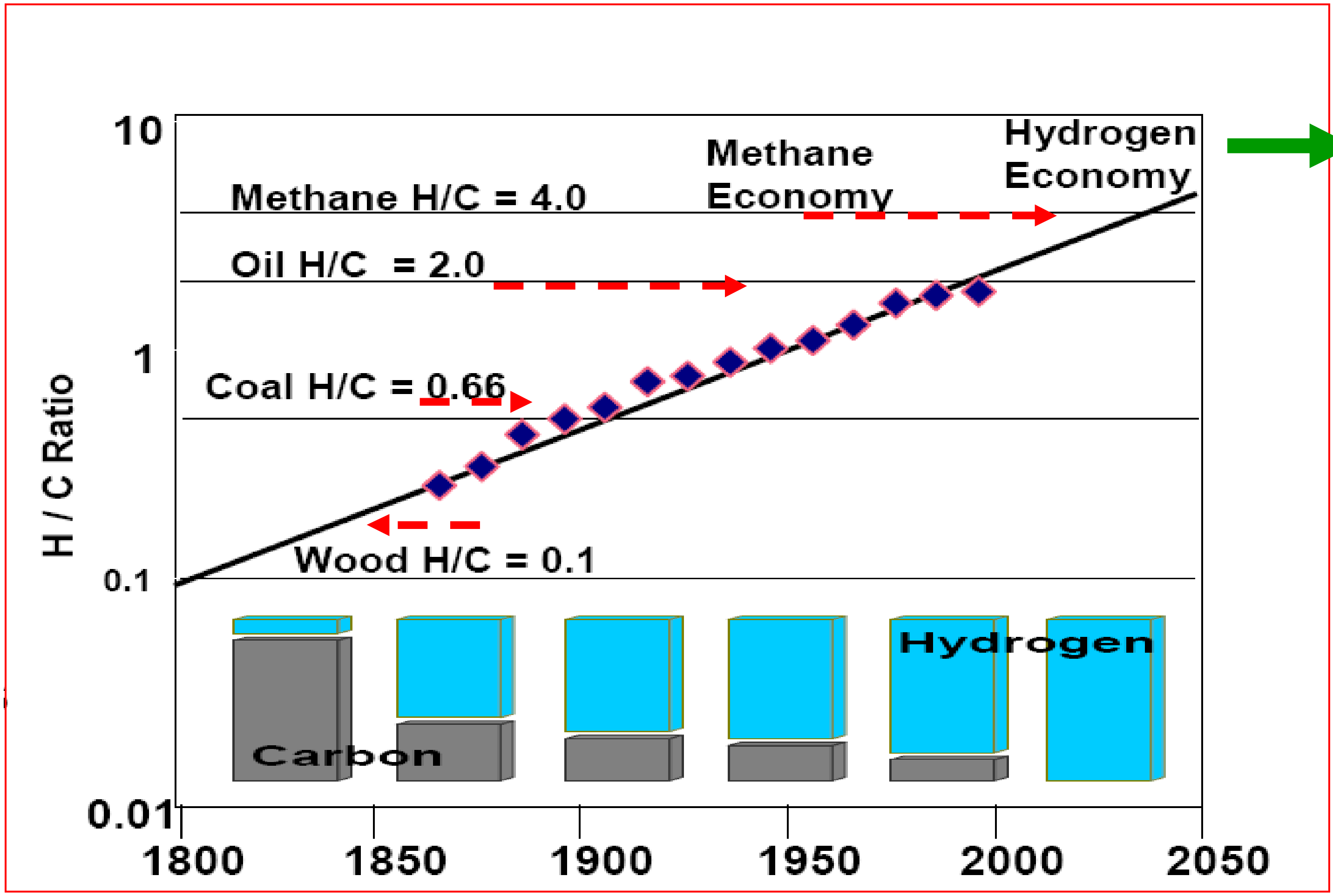
* 2005, range of study of AOP II *(Bechtel consultants)*.

Hydro – dearomatisation (HDA)



Trend in global energy consumption

'Freeing Energy from Carbon'



Fuel cell for electric power!
No more C

N. Nakicenovic, 1996

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Energy density of fuels

Fuel	MJ/kg	MJ/l	
compressed natural gas at 200 bar	53.6	10	
gasoline	46.9	34.6	Fossil
diesel fuel / residential heating oil	45.8	38.7	
polyethylene plastic	46.3	42.6	
anthracite coal	32.5	72.4	
ethanol	26.8	21.2	
methanol	19.7	15.6	Bio
sugars, carbohydrates & proteins	17	26.2	
liquid hydrogen	120	8	H_2
compressed gaseous hydrogen at 700 bar	120	4.7	
hydrogen gas	120	0.01079	

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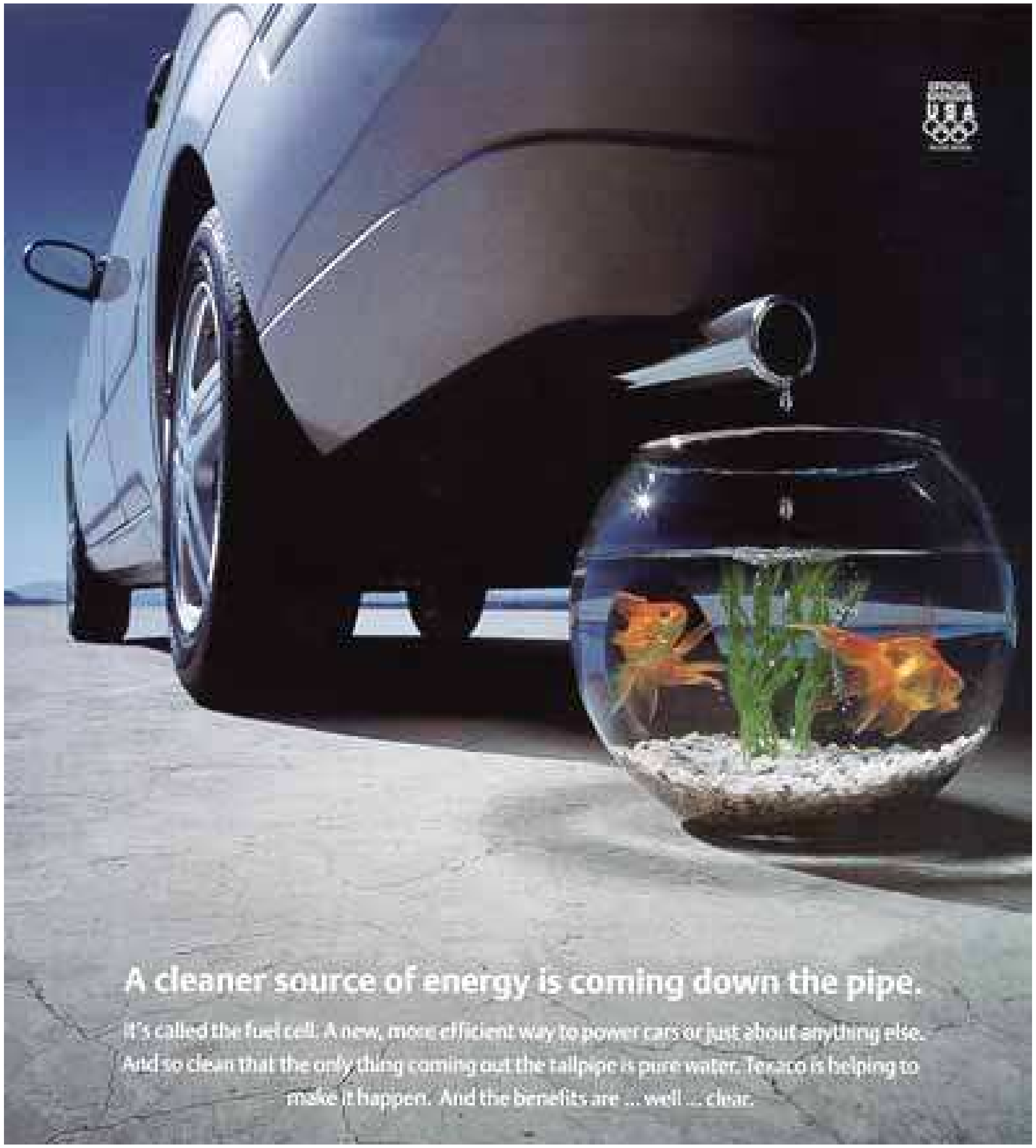
Hydrogen as a fuel

$H_2 + ½ O_2 \rightarrow$

$\rightarrow H_2O + 286$ kJ/mol

(higher heating value, i.e. after condensation of the water at 25 ^oC)



Only H_2+ ½ $O_2 \rightarrow H_2O$ + 286 kJ/mol?

Direct combustion of hydrogen in air can produce some NO_x:
At temperatures of 1600 °C some side reactions can take place:

$N_2 + O \rightarrow NO + N$
$N + O_2 \rightarrow NO + O$ Note: NO_x are severe Greenhouse gasses
$N + OH \rightarrow NO + H$

H_2 in air has a flame of ~2500 °C.
H_2 in combustion engine reaches much lower temperatures, however. The reaction time can be shortened by engine modifications in order to reduce NO_x production.

- a fuel cell does not produce NO_x

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Pure hydrogen phase behaviour

Hydrogen gas and liquid

The boiling point of hydrogen is extremely low: 20K (-253 ^oC) at 1Bar. This is because the van der Waals interaction responsible for condensation into liquid is very small for hydrogen.

Van der Waals equation for gasses:

$$\left[p + \frac{n^2}{V^2} \cdot a\right](V - n \cdot b) = nRT$$

With R=8.314 J/Kmol, a=2.476 $10^{-2} m^6 Pa/mol^2$
b=2.661 10^{-5} m^3/mol

a: related to van der Waals attraction between molecules
b: correction for small volumes, related to finite size of molecules

$$\left[p + \frac{n^2}{V^2} \cdot a\right](V - n \cdot b) = nRT$$

Note: if a,b would have been zero: just ideal gas law $pV=nRT$

$a \rightarrow$ attraction: for the same nRT and V it reduces value p
$b \rightarrow$ volume of particle: for the same nRT and p it increases the required volume.

Van der Waals constants

	a **(L^{2}bar/mol^2)**	***b*** **(L/mol)**
Argon	1.363	0.03219
Carbon dioxide	3.640	0.04267
Ethane	5.562	0.0638
Helium	0.03457	0.0237
Hydrogen	0.2476	0.02661
Methane	2.283	0.04278
Neon	0.2135	0.01709
Nitrogen	1.408	0.03913
Oxygen	1.378	0.03183
Propane	8.779	0.08445
Water	5.536	0.03049
Xenon	4.250	0.05105

Low value explains low boiling T of H_2

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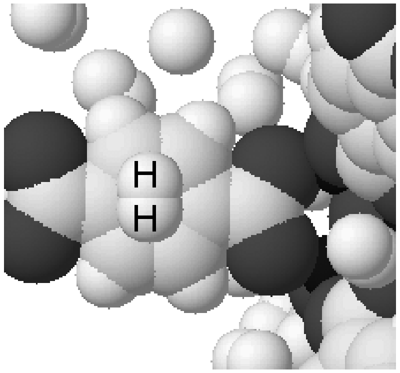

In general
- van der Waals attractions: responsible for e.g. adsorption of hydrogen molecule on surface
- van der Waals radii: approximate size of atoms

JD van de Waals
Noble prize in Physics 1910

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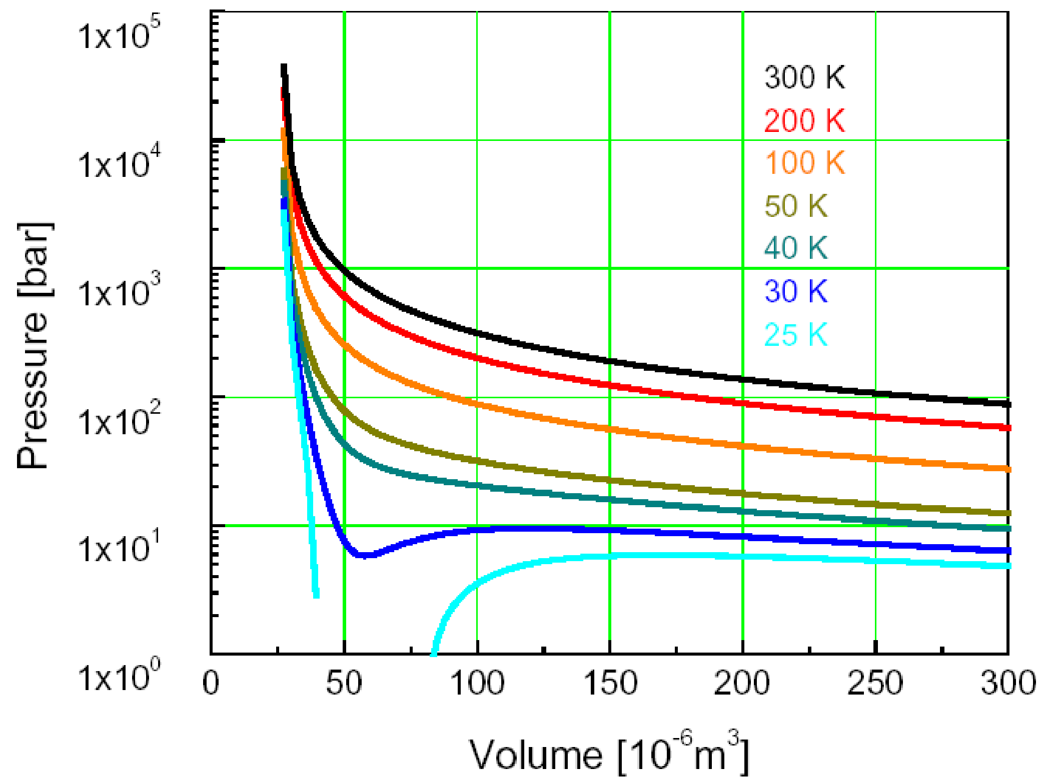
Isotherms

$$p(V) = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

not everywhere physical meaningful: negative pressures, or lowering pressure when reducing volume



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For this reason: extra stability condition:

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} < 0$$ so pressure has to increase when V is reduced

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} = -\frac{N^2 kT}{(V-nb)^2} + \frac{2N^2 a}{V^3}$$

- If T is large enough, the first term dominates; system is always stable
- If T is small, first term wins only for $V \sim nb$ and $V \to \infty$, system is unstable at intermediate V!
- Borderline case: $dp/dV = 0$ just in *one* point (critical point *K*)

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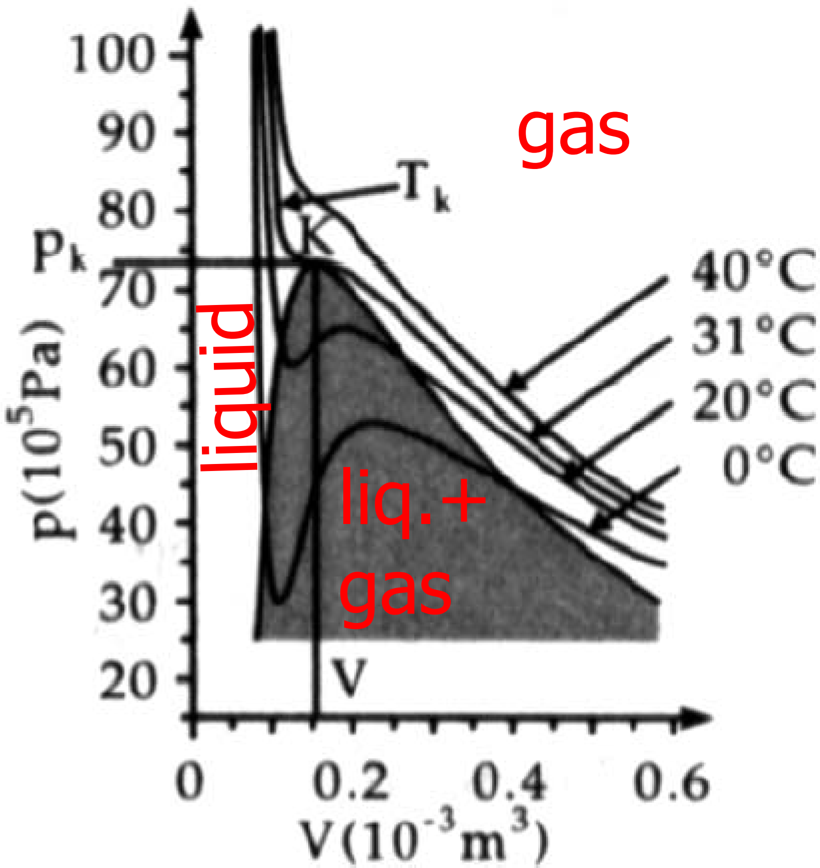
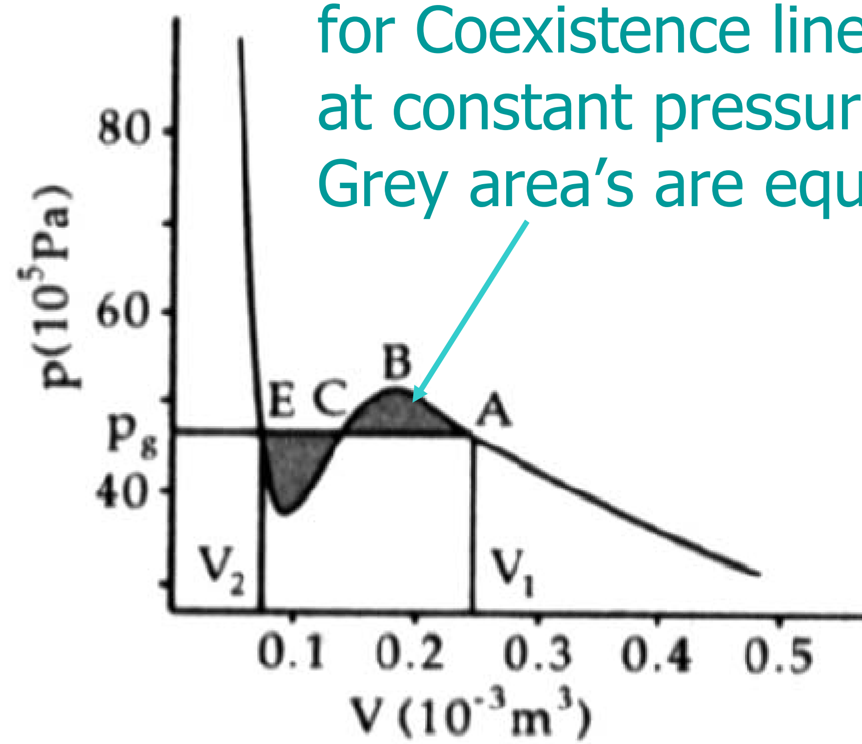
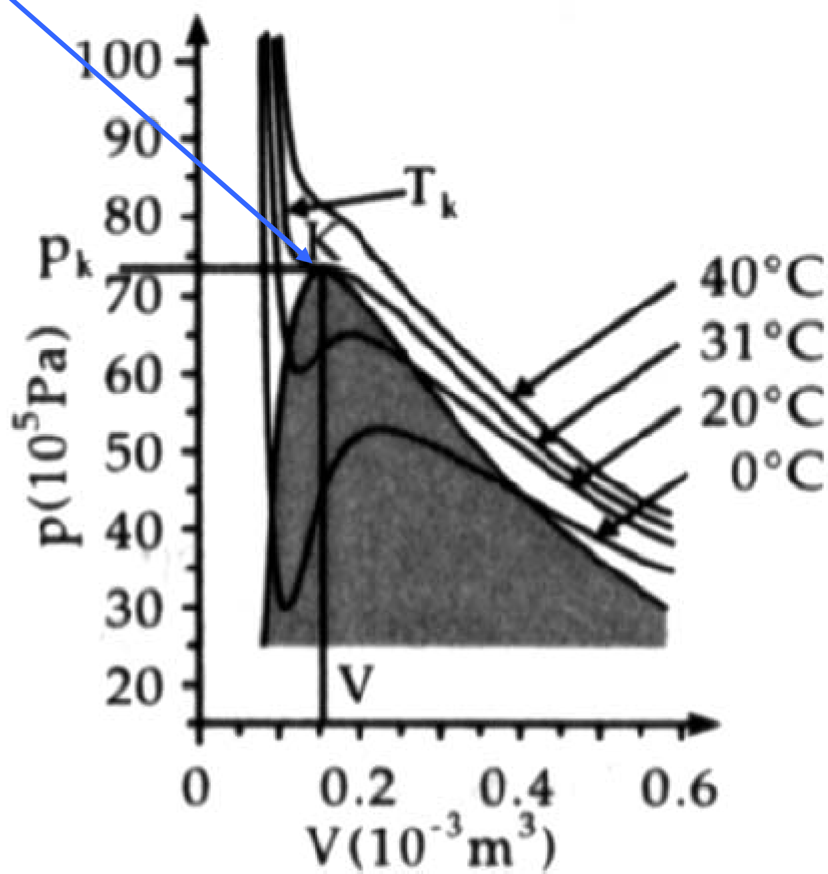


Maxwell construction for Coexistence line at constant pressure Grey area's are equal

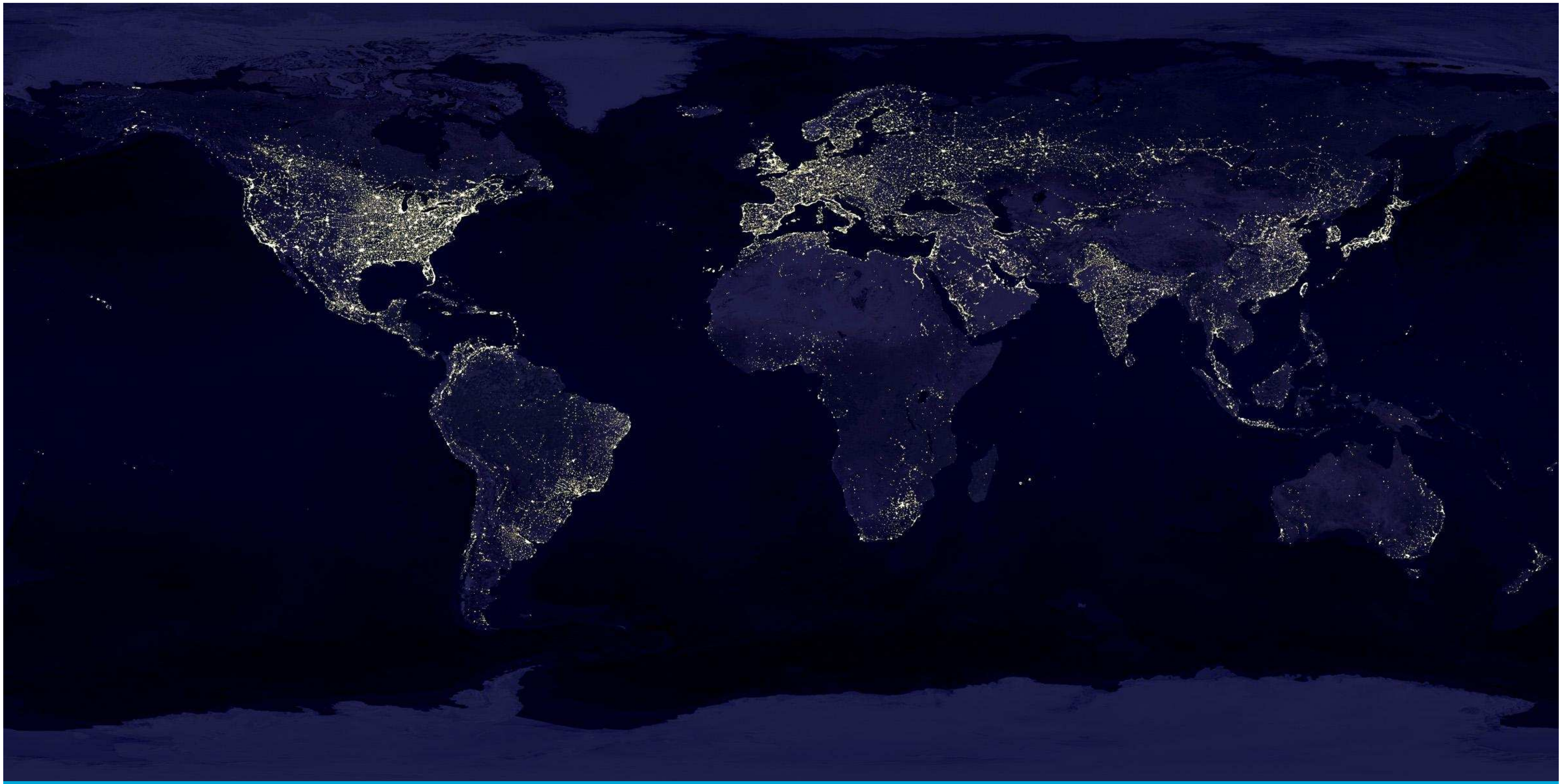


In the dark area there is coexistence of two phases: liquid and gas: changing the volume does not change pressure but changes amount of liquid versus gas

Critical point for hydrogen: 33.25 K, 12.93 Bar
Above this temperature there is no difference between gas and liquid.



Hydrogen and Electrical Energy Storage



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