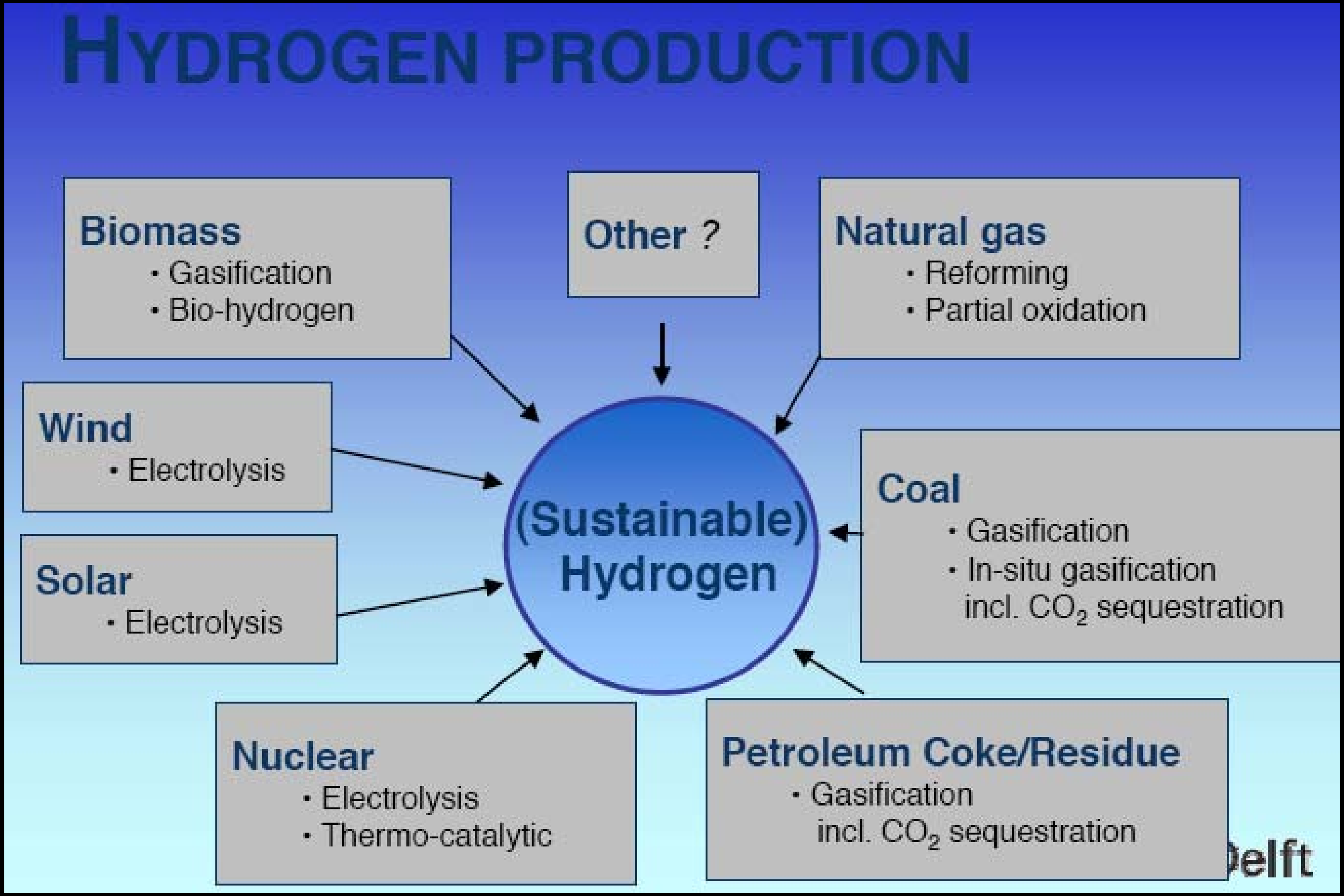
Hydrogen Production

Hydrogen Production



HYDROGEN PRODUCTION

Biomass
- Gasification
- Bio-hydrogen

Other ?

Natural gas
- Reforming
- Partial oxidation

Wind
- Electrolysis

Solar
- Electrolysis

(Sustainable) Hydrogen

Coal
- Gasification
- In-situ gasification incl. CO_2 sequestration

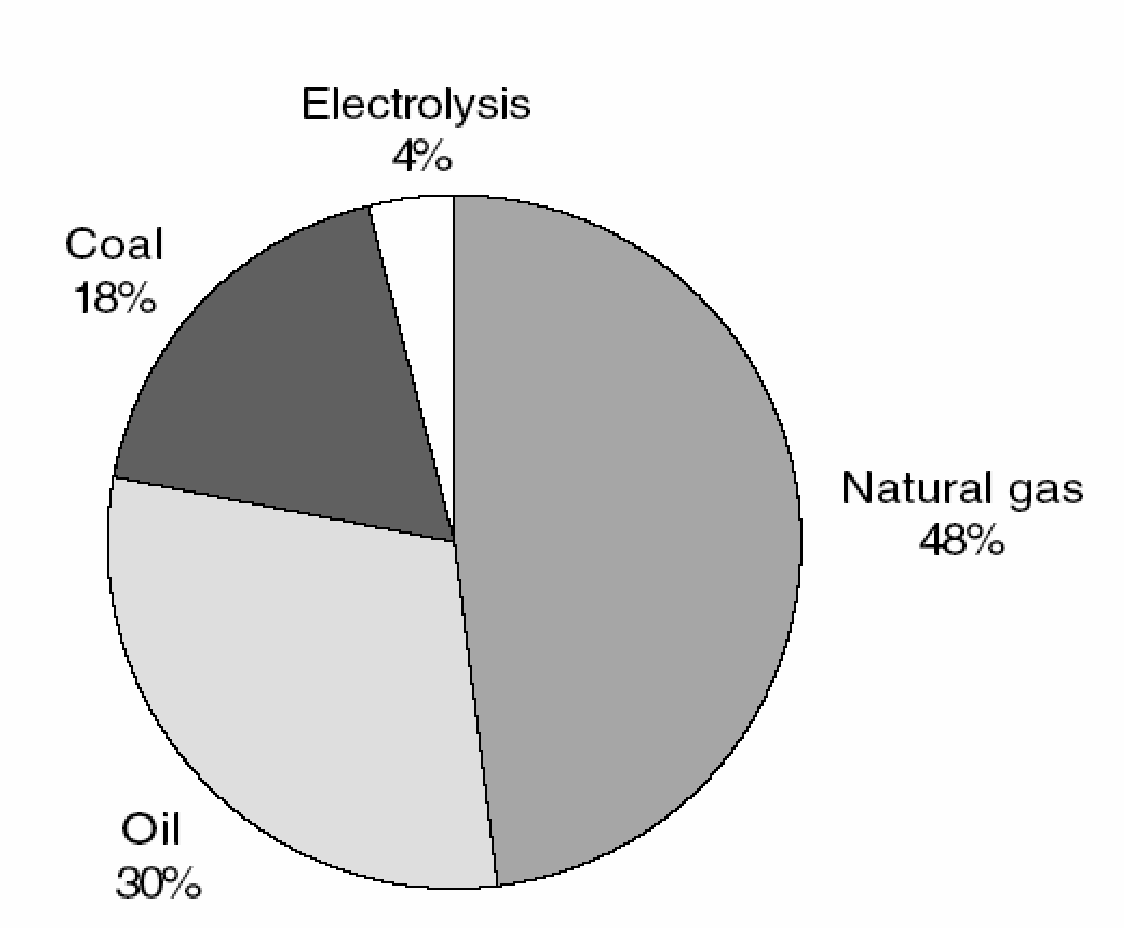
Nuclear
- Electrolysis
- Thermo-catalytic

Petroleum Coke/Residue
- Gasification incl. CO_2 sequestration

elft

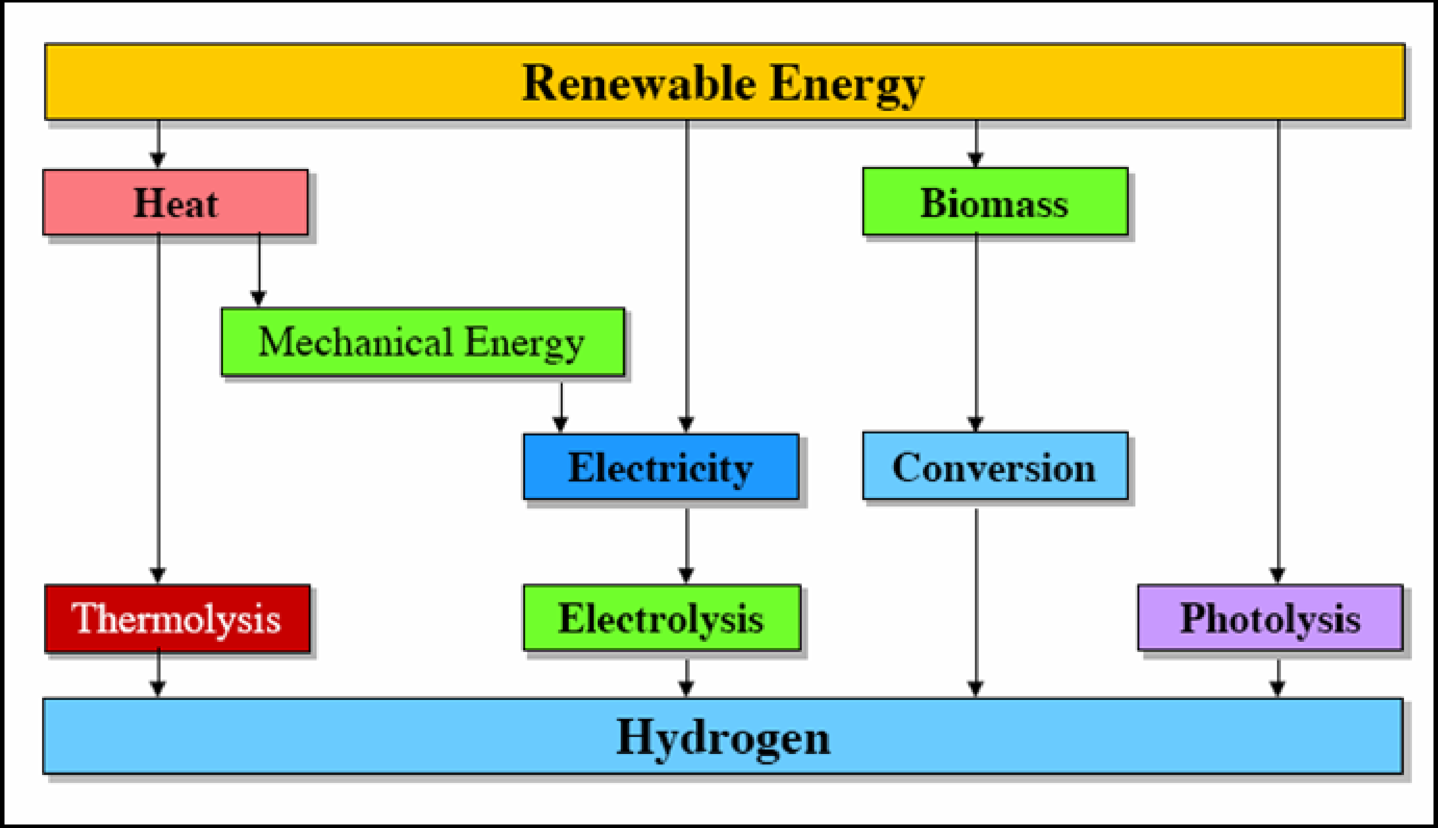
Source: Prof.Dr. J. Schoonman
Delft Institute for Sustainable Energy

Feedstocks Usage in Hydrogen Production



Source: NAS Study, 2004

Sustainable Paths to Hydrogen



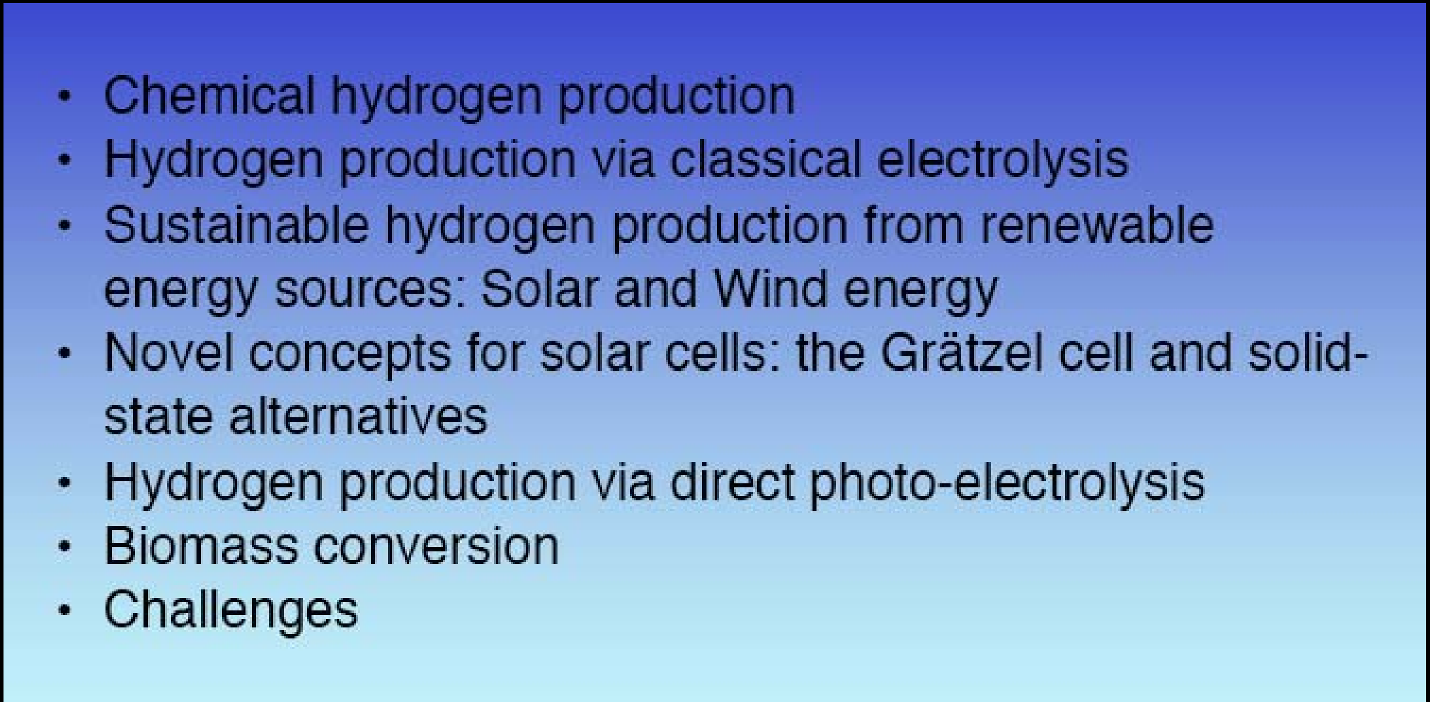
Source: D. Brent MacQueen
Brent.macqueen@sri.com
SRI International, Menlo Park CA

Hydrogen Production Methods

Most methods of producing hydrogen involve splitting water (H_2O) into its component parts of hydrogen (H_2) and oxygen (O). The most common method involves steam reforming of methane (from natural gas), although there are several other methods.

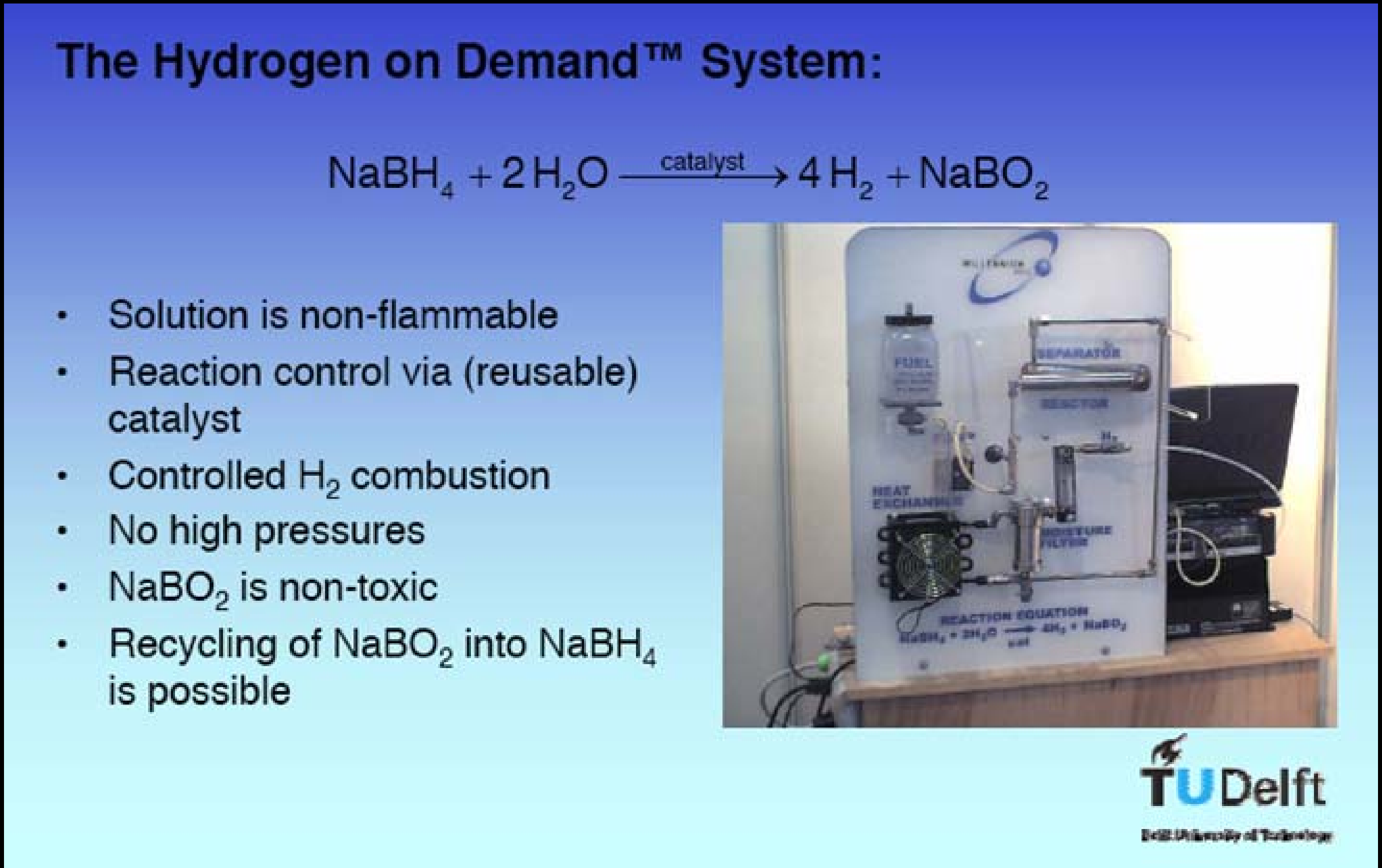
- Steam reforming converts methane (and other hydrocarbons in natural gas) into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst
- Electrolysis uses electrical current to split water into hydrogen at the cathode (+) and oxygen at the anode (-)
- Steam electrolysis (a variation on conventional electrolysis) uses heat, instead of electricity, to provide some of the energy needed to split water, making the process more energy efficient
- Thermochemical water splitting uses chemicals and heat in multiple steps to split water into its component parts
- Photoelectrochemical systems use semi-conducting materials (like photovoltaics) to split water using only sunlight
- Photobiological systems use microorganisms to split water using sunlight
- Biological systems use microbes to break down a variety of biomass feed stocks into hydrogen
- Thermal water splitting uses a very high temperature (approximately 1000°C) to split water
- Gasification uses heat to break down biomass or coal into a gas from which pure hydrogen can be generated

Hydrogen Production



- Chemical hydrogen production
- Hydrogen production via classical electrolysis
- Sustainable hydrogen production from renewable energy sources: Solar and Wind energy
- Novel concepts for solar cells: the Grätzel cell and solid-state alternatives
- Hydrogen production via direct photo-electrolysis
- Biomass conversion
- Challenges

Chemical Hydrogen Production



The Hydrogen on Demand™ System:

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} 4H_2 + NaBO_2$$

- Solution is non-flammable
- Reaction control via (reusable) catalyst
- Controlled H_2 combustion
- No high pressures
- $NaBO_2$ is non-toxic
- Recycling of $NaBO_2$ into $NaBH_4$ is possible

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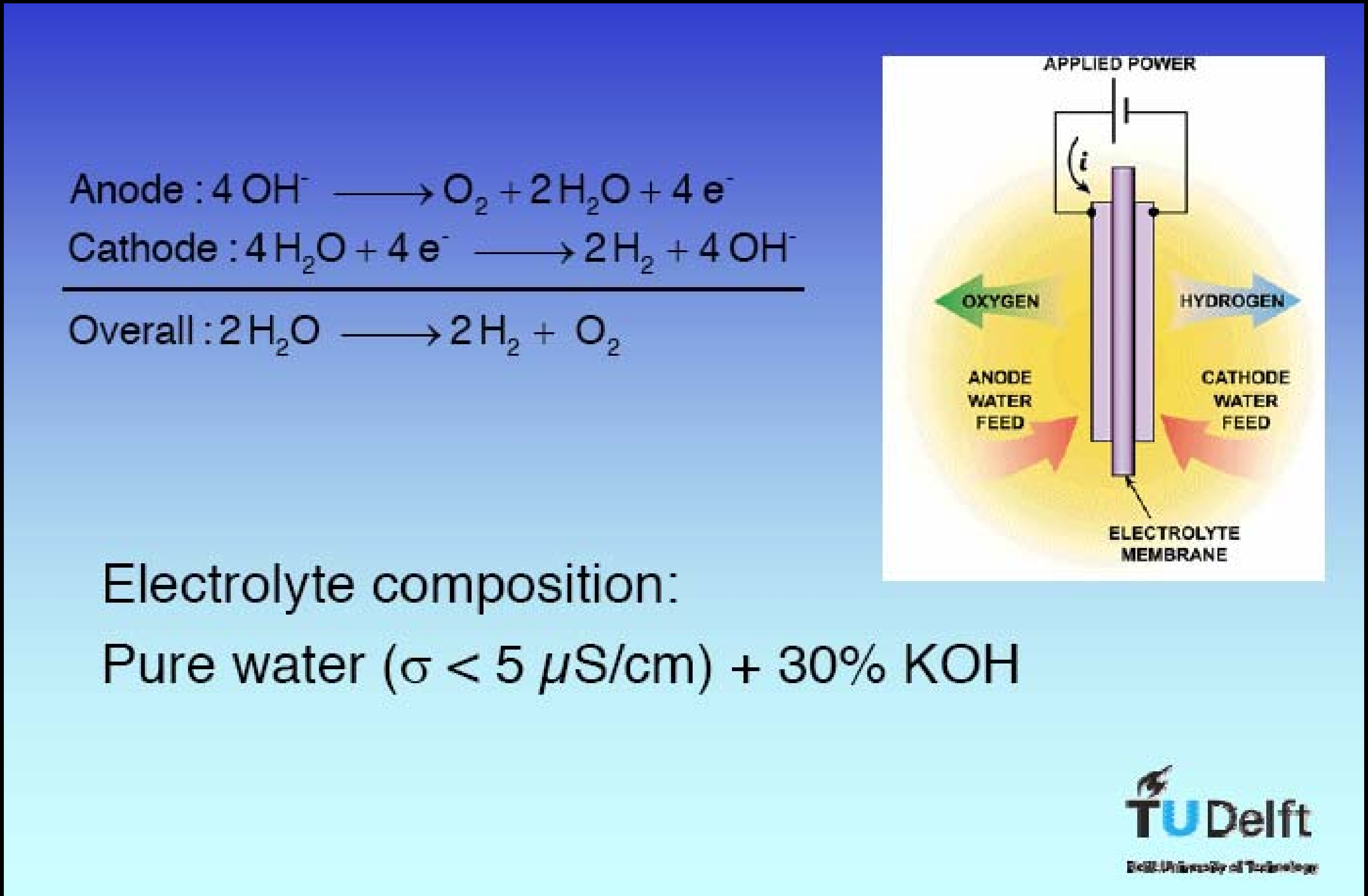
Electrolysis



$$\text{Anode}: 4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-$$

$$\text{Cathode}: 4\,H_2O + 4\,e^- \longrightarrow 2\,H_2 + 4\,OH^-$$

$$\text{Overall}: 2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Electrolyte composition:

Pure water ($\sigma < 5\ \mu S/cm$) + 30% KOH

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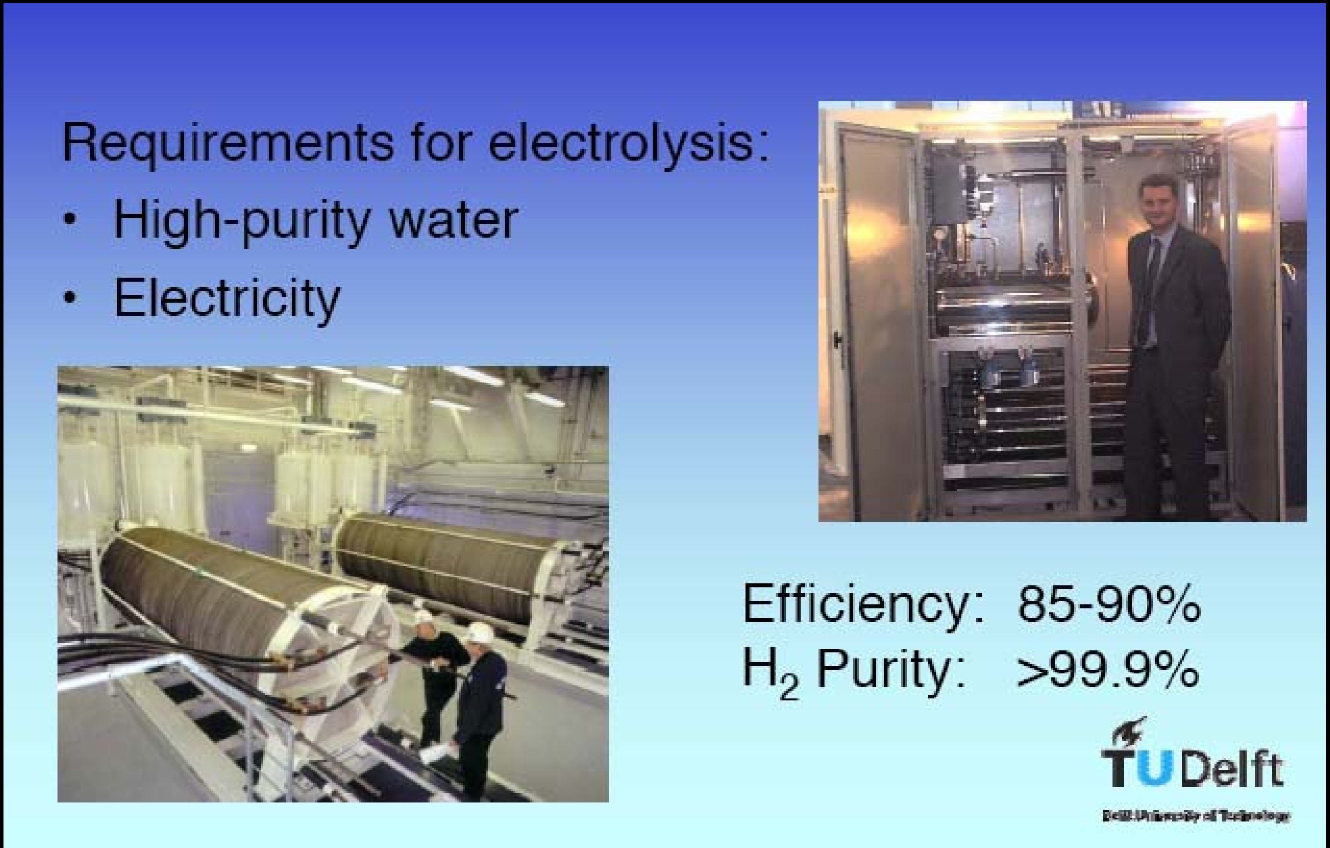
Electrolysis



Requirements for electrolysis:

- High-purity water
- Electricity

Efficiency: 85-90%

H_2 Purity: >99.9%

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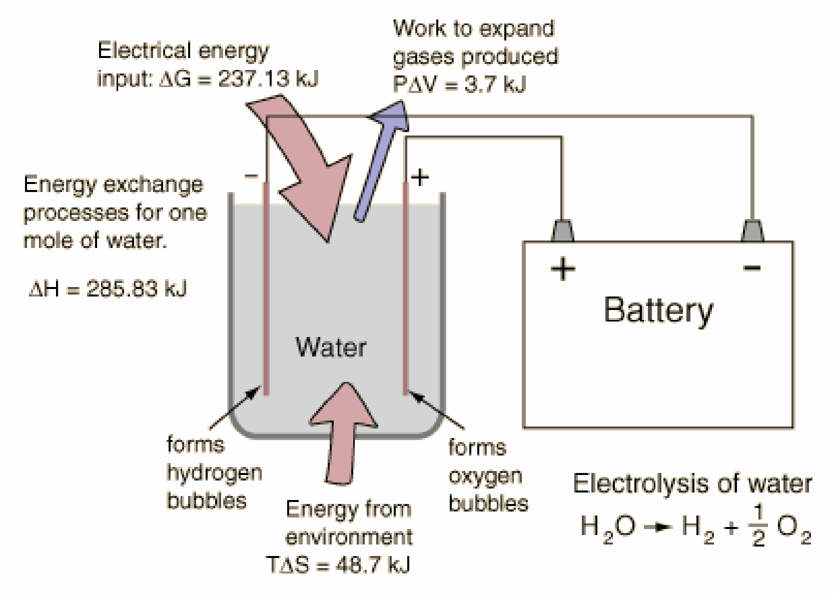
Electrolysis of Water



By providing energy from a battery, water (H_2O) can be dissociated into the diatomic molecules of hydrogen (H_2) and oxygen (O_2). This process is a good example of the the application of the four thermodynamic potentials (internal energy, U, Helmoltz free energy, F = U-TS; Enthalpy, H = U+pv and Gibbs free energy, G =U+pv-TS.

The electrolysis of one mole of water produces a mole of hydrogen gas and a half a mole of oxygen gas in their normal diatomic forms. A detailed analysis of this process makes use of the thermodynamic potentials and the first law of thermodynamics. This process is presumed to be at 298K and atmospheric pressure.

Electrolysis of Water

System work:

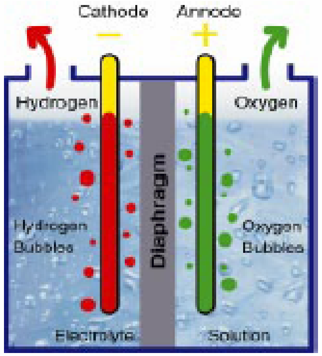
Quanitity	H_2O	H_2	$0.5O_2$	Change
Enthalpy	-285.83kJ	0	0	$\Delta H = -285.83\text{kJ}$
Entropy	69.91 J/K	130.68J/K	0.5x205.14J/K	$T\Delta S = 48.7$ kJ

$W = P\Delta V = (101.3\text{ kPa})(1.5\text{ moles})(22.4\text{x}10^{-3}\text{m}^3/\text{mol})(298\text{K}/273\text{K}) = 3715\text{ J}$

$\Delta U = \Delta H\text{-}P\ \Delta V = 285.83\text{kJ}-3.72\text{ kJ} = 282.1\text{ kJ}$

$\Delta G = \Delta H\text{-}T\ \Delta S = 285.83\text{ kJ}-48.7\text{ kJ} = 237.1\text{ kJ}$

Efficiency



- Energy efficiency of electrolysis =

$$\frac{\text{Chemical potential}}{\text{Electrolysis potential}} = \frac{1.23}{1.9} = 65\%$$

Systems that claim 85 %

- Coupling to a 12% PV array gives a solar-to-hydrogen efficiency of:

$$.12^{*}.65 = 7.8\%$$

Improved electrolysis efficiency can bring the PV-hydrogen efficiency to about 10%

Hydrogen Production

Reaction:

$$H_2\,(g) + O_2\,(g) \leftrightarrow H_2O\,(l) + 286\ \text{kJ/mole}$$

Global energy demand: $4x10^{20}$ J/year

H_2 from water: 1 GJ per 90 liters H_2O

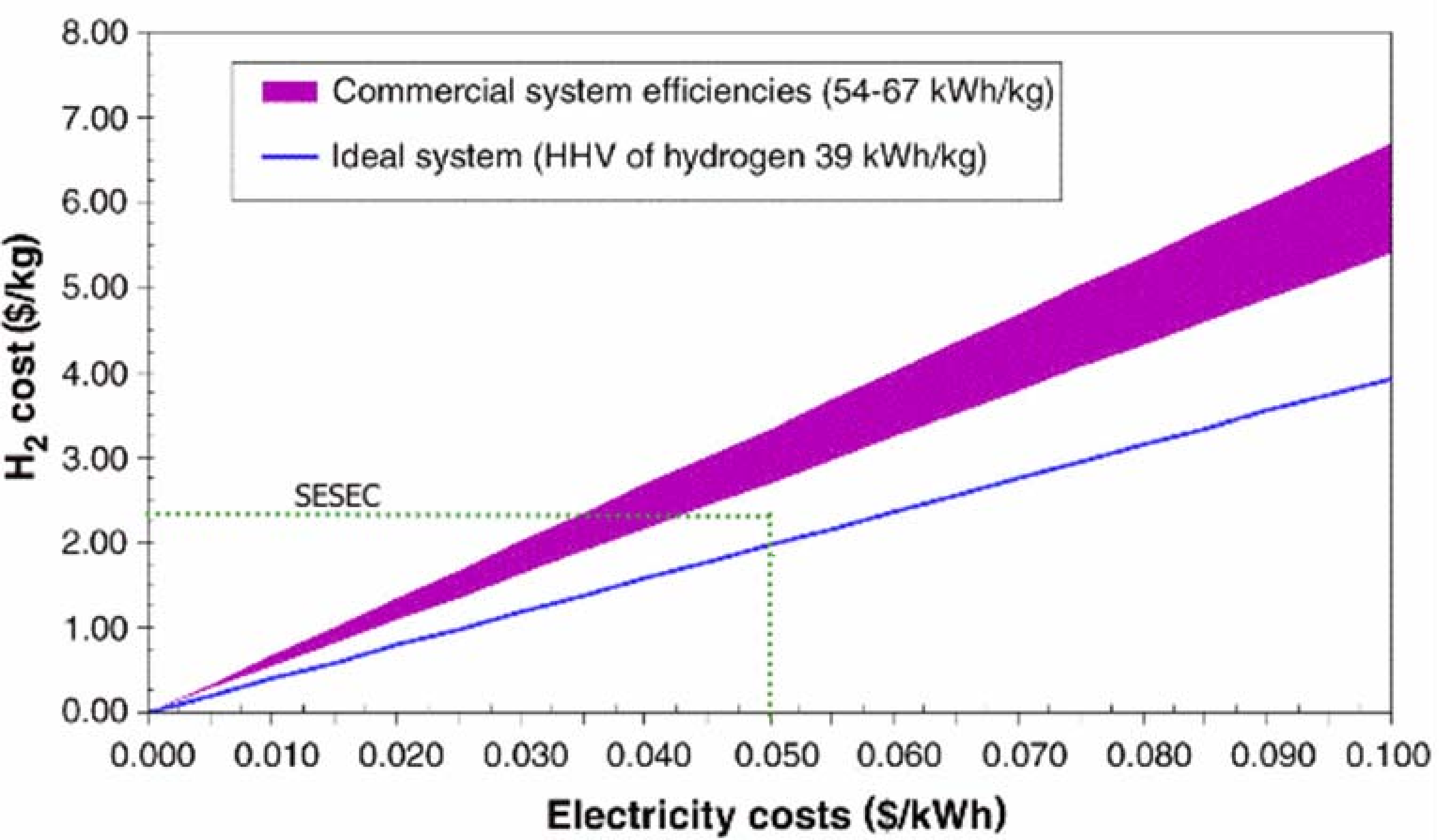
Water needed: $3.6x10^{13}$ liters

Oceans: $1.45x10^{21}$ liters

Annual rainfall: $3.62x10^{17}$ liters

There is enough water to sustain hydrogen!

Hydrogen-Electricity



Electrolysis of Water

LOW CURRENT ELECTROLYSIS OF WATER by **Ph. M. Kanarev**

The most modern Electrolyzers consume 4.0 kWh per cubic meter of H_2 gas. Electrolysis process takes place by voltage of 1.6-2.0 V and current strength of dozens and hundreds of amperes. When one cubic meter of hydrogen is burnt, 3.55 kWh of energy is released [1].

A money-saving process of decomposition of water molecules into hydrogen and oxygen exists in the nature. This process takes place during photosynthesis. Hydrogen atoms are separated from water molecules and are used as connecting links while forming organic molecules, and oxygen is released into the air.

A question emerges: is it possible to model an electrolytical process of water decomposition into hydrogen and oxygen, which takes place during photosynthesis? A search of a reply to this question has resulted in a simple structure of a cell (Fig. 1), in which the process takes place by voltage of 1.5-2.0 V between the anode and the cathode and amperage of 0.02 amperes [1], [2].

http://guns.connect.fi/innoplaza/energy/story/Kanarev/electrolysis/

Hydrogen Production

The electrodes of the cell are made of steel. It helps to avoid the phenomena, which are appropriate to a galvanic cell. Nevertheless, at the cell electrodes a potential difference of nearly 0.1 V takes place in complete default of electrolytic solution in it. When the solution is charged, the potential difference is increased. The positive sign of the charge appears on the upper electrode always, and the negative sign appears on the lower one. If a direct current source generates pulses, gas output is increased.

As a laboratory model of the low current electrolyzer cell generates small quantity of gases, a solution mass change definition method during the experiment and further calculation of released hydrogen and oxygen is the most reliable method of definition of their quantity.

It is known that a gram atom is equal to atomic mass of substance; a gram molecule is equal to molecular mass of substance. For example, the gram molecule of hydrogen in the water molecule is equal to two grams; the gram-atom of the oxygen atom is 16 grams. The gram molecule of water is equal to 18 grams. Hydrogen mass in a water molecule is 2x100/18=11.11%; oxygen mass is 16x100/18=88.89%; this ratio of hydrogen and oxygen is in one liter of water. It means that 111.11 grams of hydrogen and 888.89 grams of oxygen are in 1000 grams of water.

One liter of hydrogen weighs 0.09 g; one liter of oxygen weighs 1.47 g. It means that it is possible to produce 111.11/0.09=1234.44 liters of hydrogen and 888.89/1.47=604.69 liters of oxygen from one liter of water. It appears from this that one gram of water contains 1.23 liters of hydrogen. Energy consumption for production of 1000 liters of hydrogen is 4 kWh and for one liter 4 Wh. As it is possible to produce 1.234 liters of hydrogen from one gram of water, 1.234x4=4.94 Wh is spent for hydrogen production from one gram of water now.

Hydrogen Production

A small value of current 0.02 A and voltage 0.062 V allows us to suppose that in the low current electrolyzer the water electrolysis process is similar to the process, which takes place during photosynthesis. At photosynthesis, hydrogen separated from the water molecule is used as a connecting link while organic molecule formation, and oxygen is released in the air. At low current electrolysis, both hydrogen and oxygen are released in the air.

Note: gas release is clearly seen during several hours after the cell is disconnected from the line.

REFERENCES

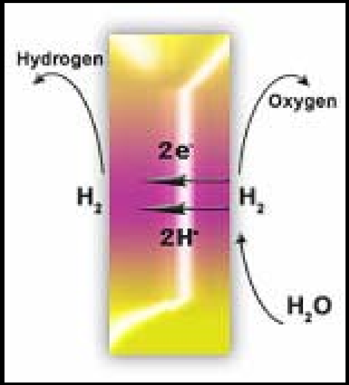
1. Kanarev Ph.M. The Foundation of Physchemistry of Microworld. The third edition. – Krasnodar: KSAU, 2003. http://Kanarev.innoplaza.net (In Russian, Part 1, Part 2).
2. Kanarev Ph.M. The Foundation of Physchemistry of Microworld. The second edition. (In English). http://book.physchemistry.innoplaza.net

Hydrogen Production

Producing hydrogen from water, without electrolysis

Electrochemical potential difference drives the reaction

Researchers at DOE’s National Energy Technology Laboratory and Argonne National Laboratory have patented a "Method of Generating Hydrogen by Catalytic Decomposition of Water." The invention potentially leapfrogs current capital and energy intensive processes that produce hydrogen from fossil fuels or through the electrolysis of water. According to co-inventor Arun Bose, "Hydrogen can be produced by electrolysis, but the high voltage requirements are a commercial barrier. The invention provides a new route for producing hydrogen from water by using mixed proton-electron conducting membranes." Water is decomposed on the feed surface. The hydrogen is ionized and protons and electrons travel concurrently through the membrane. On the permeate side, they combine into hydrogen molecules.



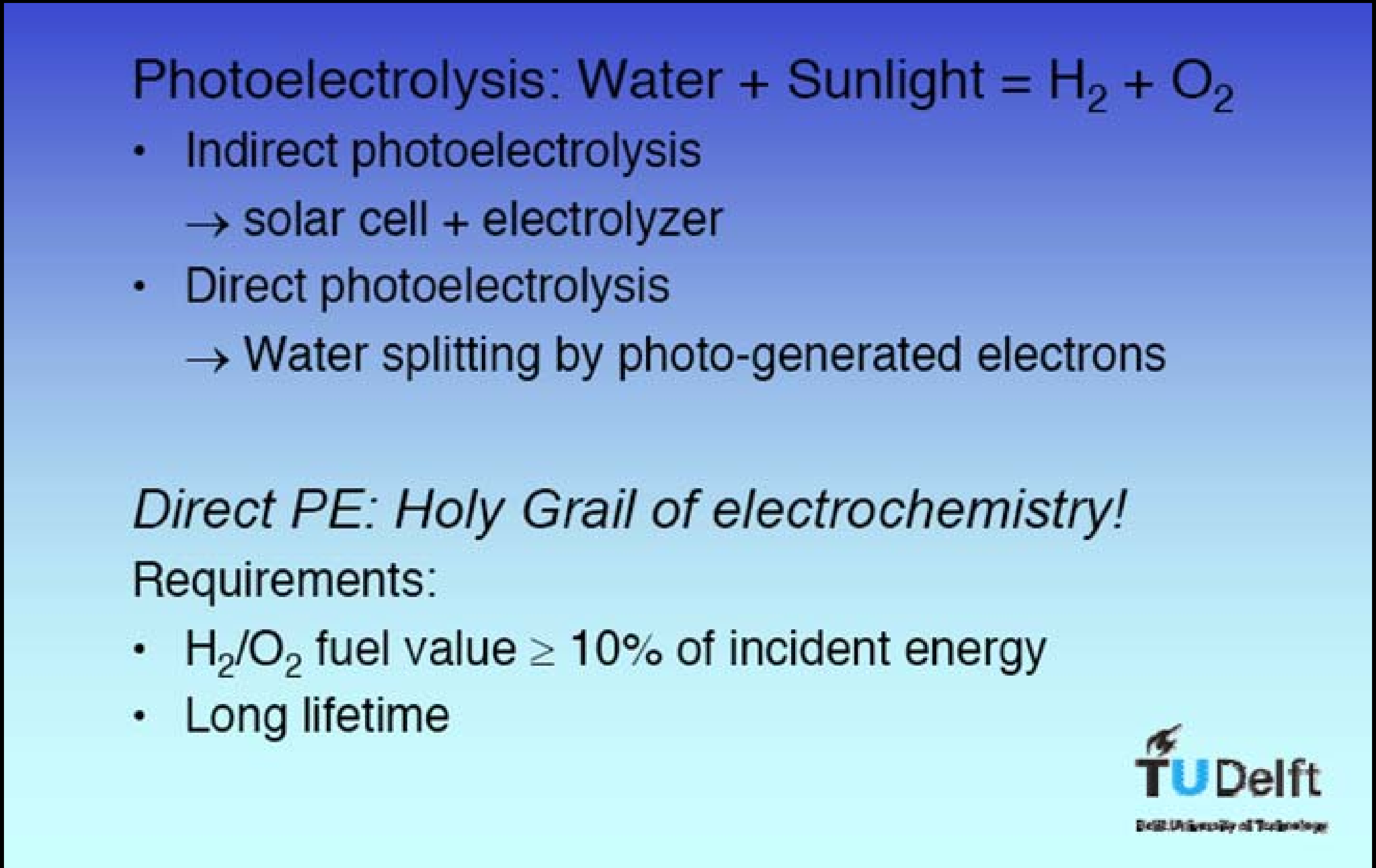
US patent # 6,468,499

Photoelectrolysis

Hydrogen Production by Photo-electrolysis of Water

The photo-electrolysis of water into hydrogen and oxygen using solar energy is potentially a clean and renewable source of hydrogen fuel for the hydrogen economy. The energy conversion efficiency of water photo-electrolysis is determined mainly by the properties of the materials used as electrodes in the photo-electrochemical cell. Obstacles to direct photo-electrolysis of water are the lack of efficient light absorption, corrosion of the semiconductor photo-catalyst and energetics. The aim of research work is to engineer materials with appropriate optical, electronic and chemical properties for use as photo-catalysts in efficient and cost effective photo-electrochemical cells.

Photoelectrolysis



Photoelectrolysis: Water + Sunlight = $H_2 + O_2$

- Indirect photoelectrolysis
  → solar cell + electrolyzer
- Direct photoelectrolysis
  → Water splitting by photo-generated electrons

Direct PE: Holy Grail of electrochemistry!

Requirements:

- H_2/O_2 fuel value ≥ 10% of incident energy
- Long lifetime

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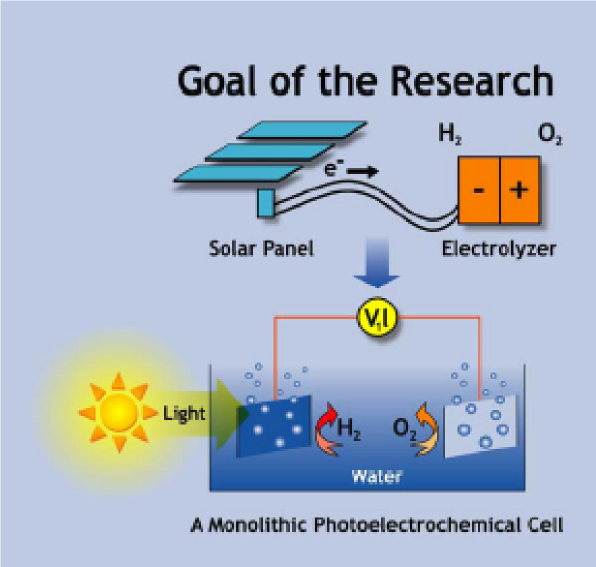
Direct Conversion

Photoelectrochemical-Based Direct Conversion Systems

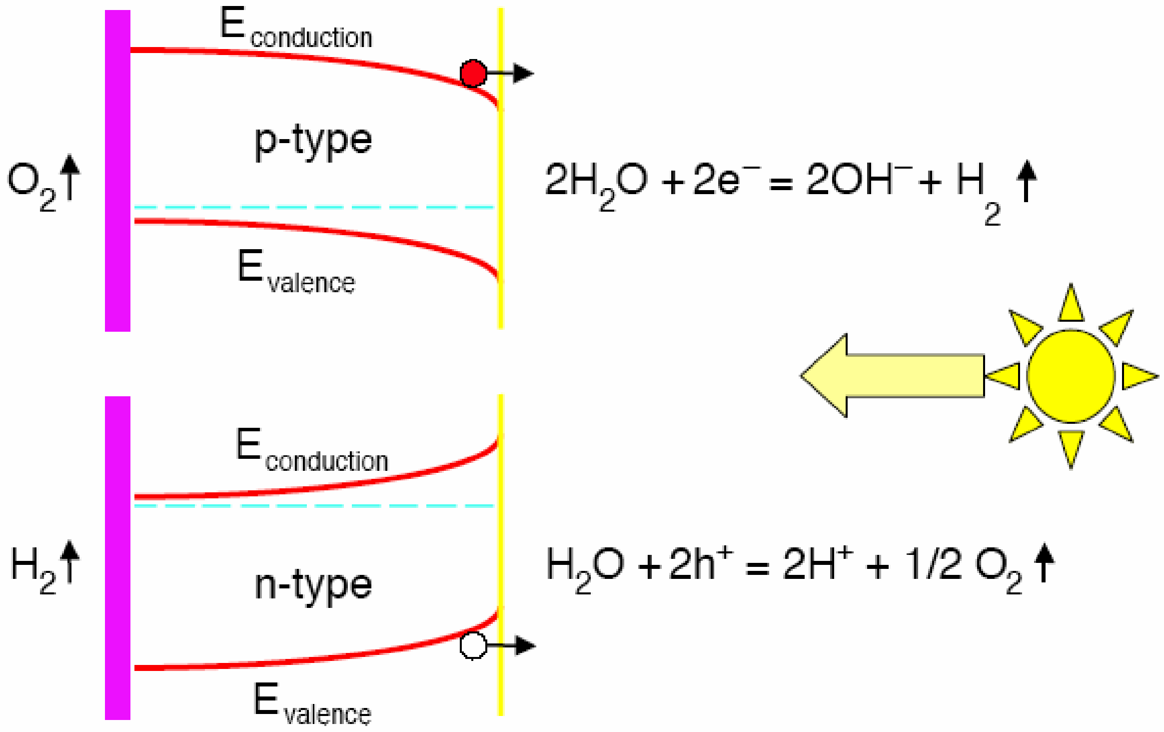


A Monolithic Photoelectrochemical Cell

- Combines a photovoltaic system (light harvesting) and an electrolyzer (water splitting) into a single monolithic device.
  - Electrolysis area approximates that of the solar cell - the current density is reduced.
- Balance of system costs reduced.
  - Capital cost of electrolyzer eliminated
- Semiconductor processing reduced.
- Efficiency 30% higher than separated system.

Photoelectrolysis

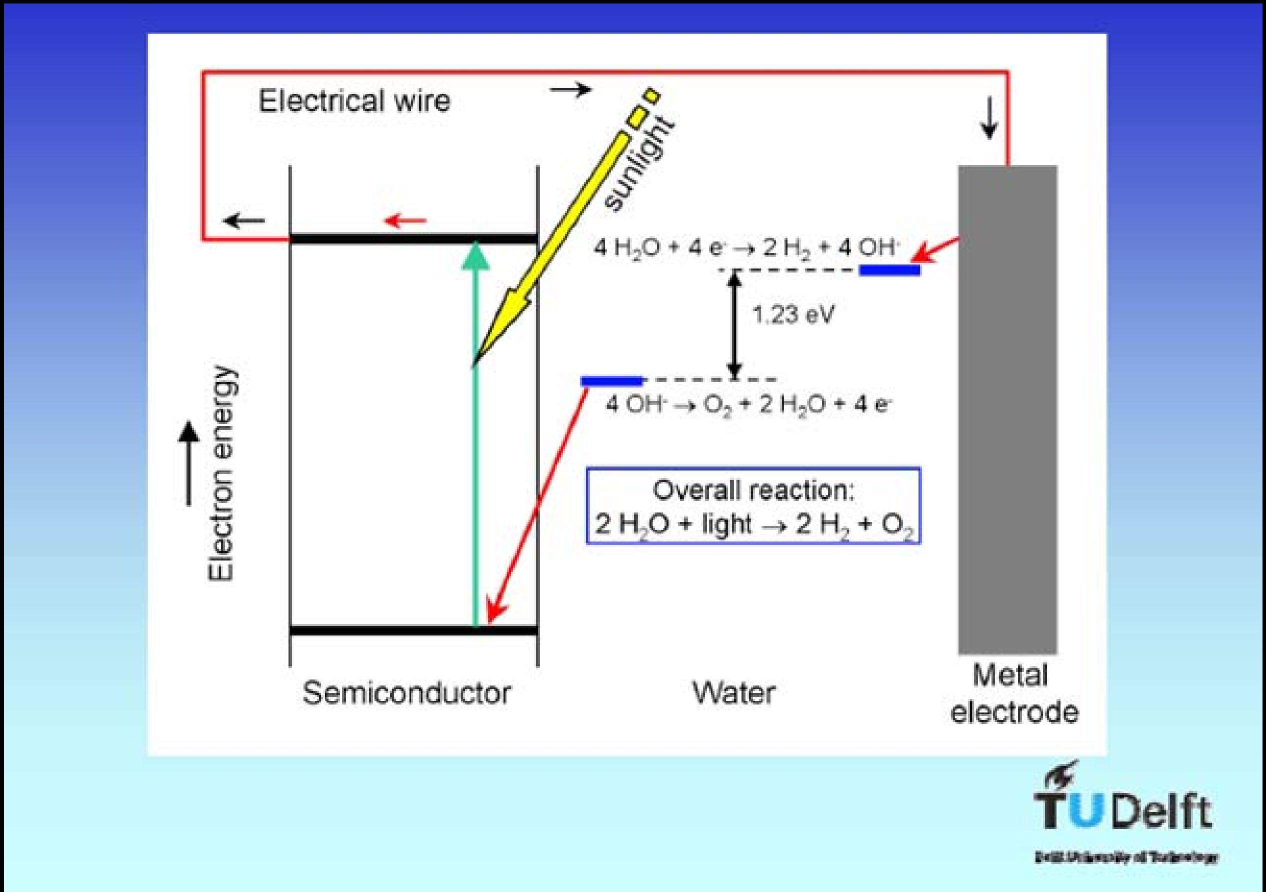
Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



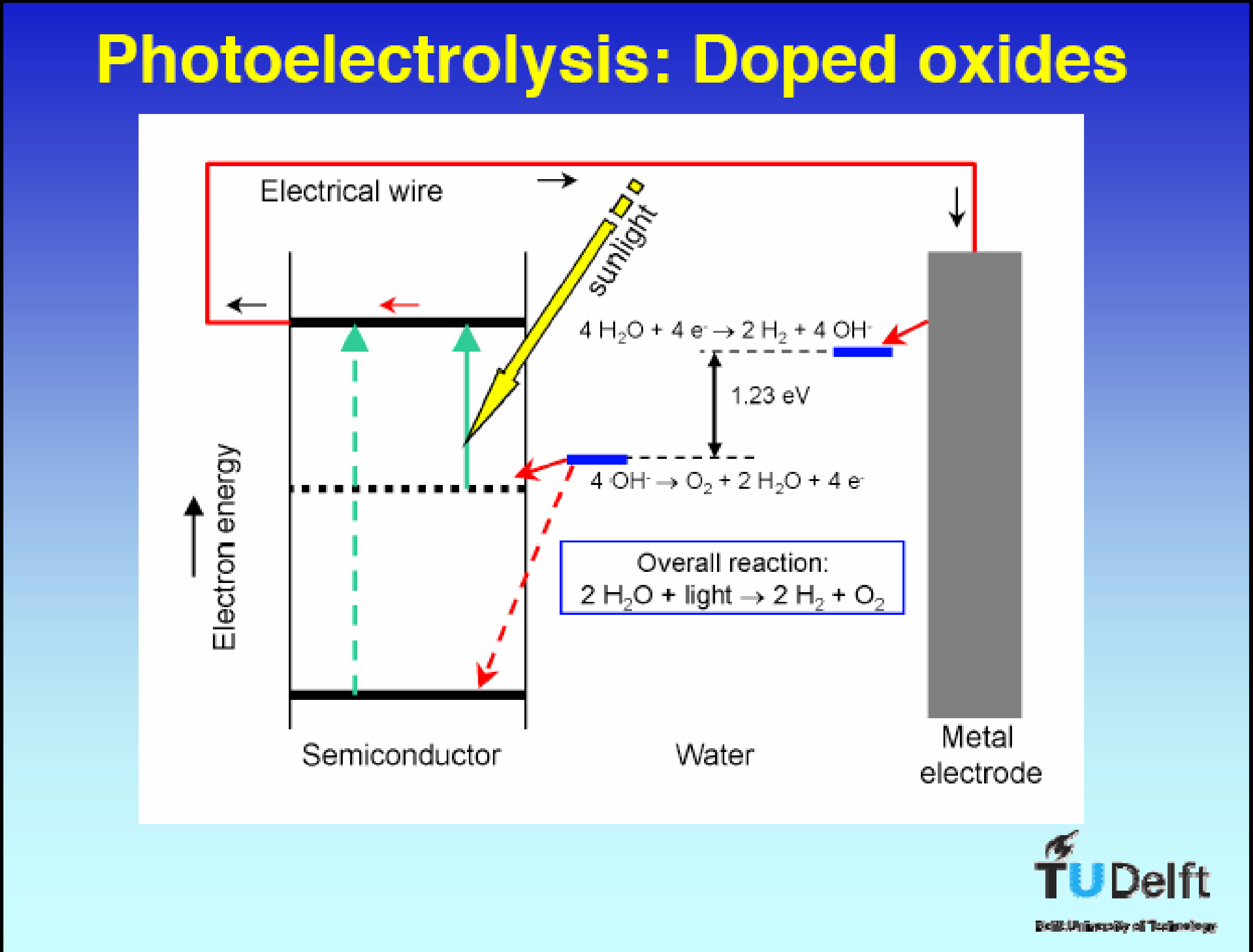
$2H_2O + 2e^- = 2OH^- + H_2\uparrow$

$H_2O + 2h^+ = 2H^+ + 1/2\ O_2\uparrow$

Photoelectrolysis



Photoelectrolysis



Photoelectrolysis: Doped oxides

$4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^-$

$4\,OH^- \rightarrow O_2 + 2\,H_2O + 4\,e^-$

Overall reaction:

$2\,H_2O + \text{light} \rightarrow 2\,H_2 + O_2$

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Photoelectrolysis

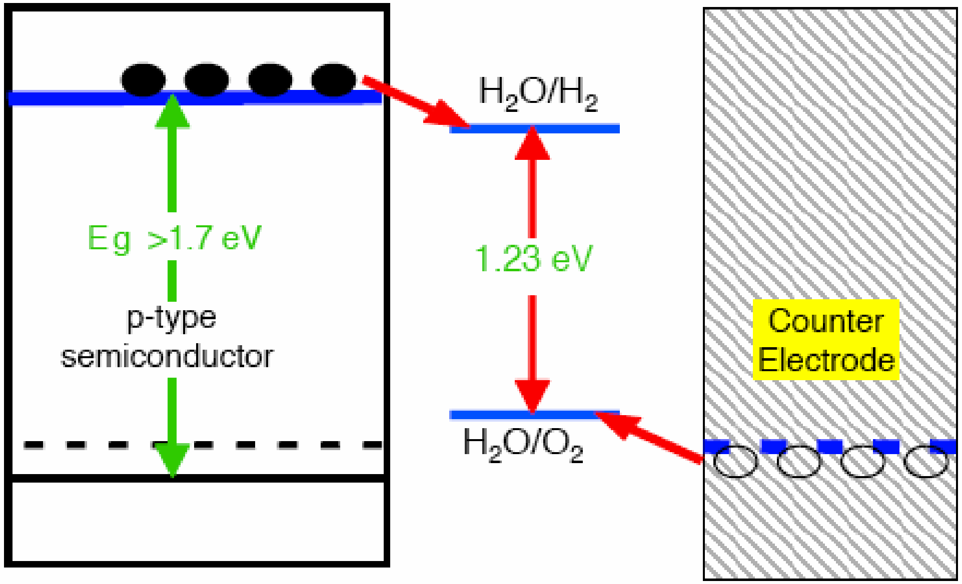
Material and Energetic Requirements

Bandgap

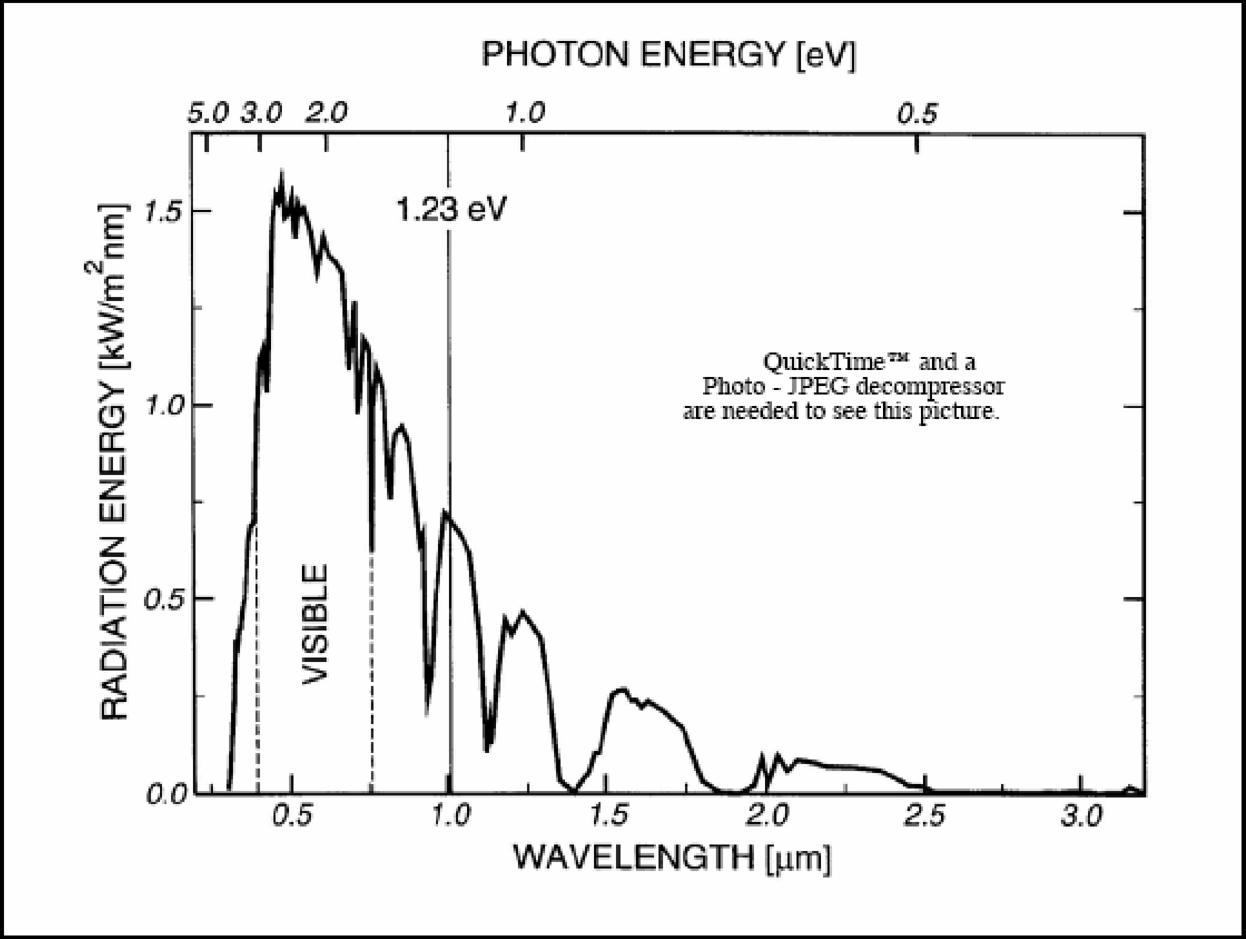
Band edge overlap

Fast charge transfer

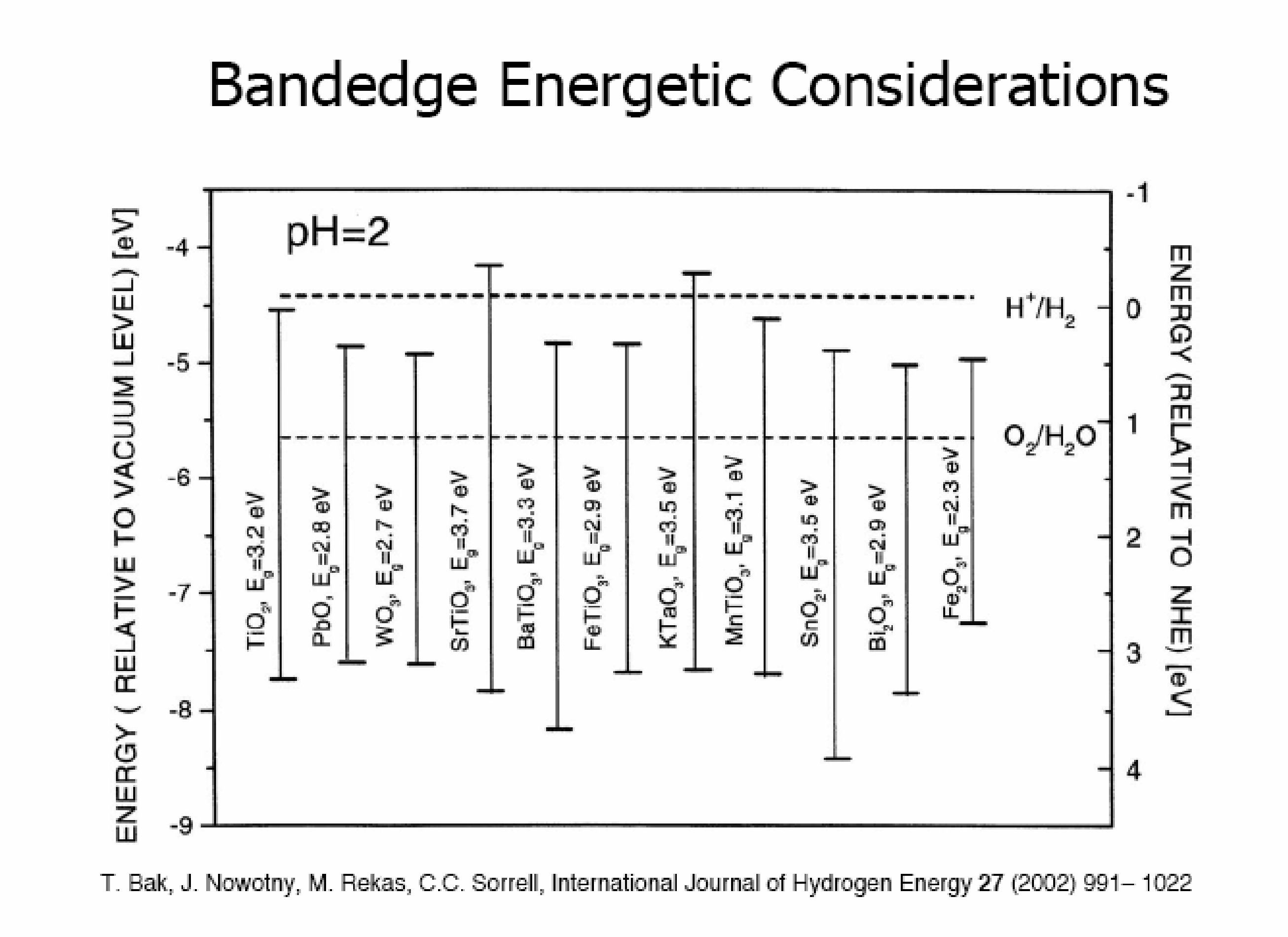
All three energetic conditions must be satisfied SIMULTANEOUSLY + ***Stability***



Bandgap Considerations



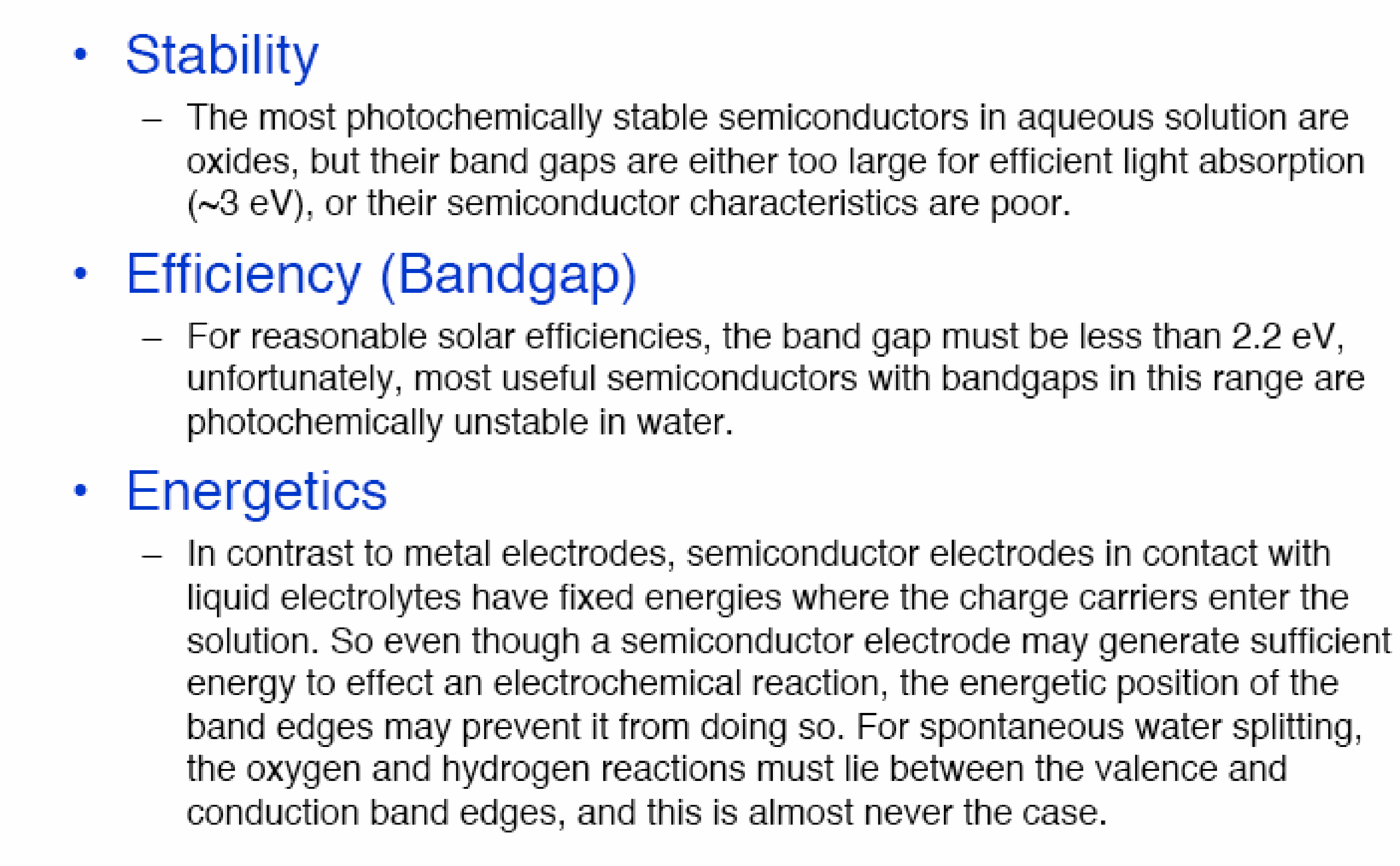
Bandedge Energetic Considerations



Bandedge Energetic Considerations

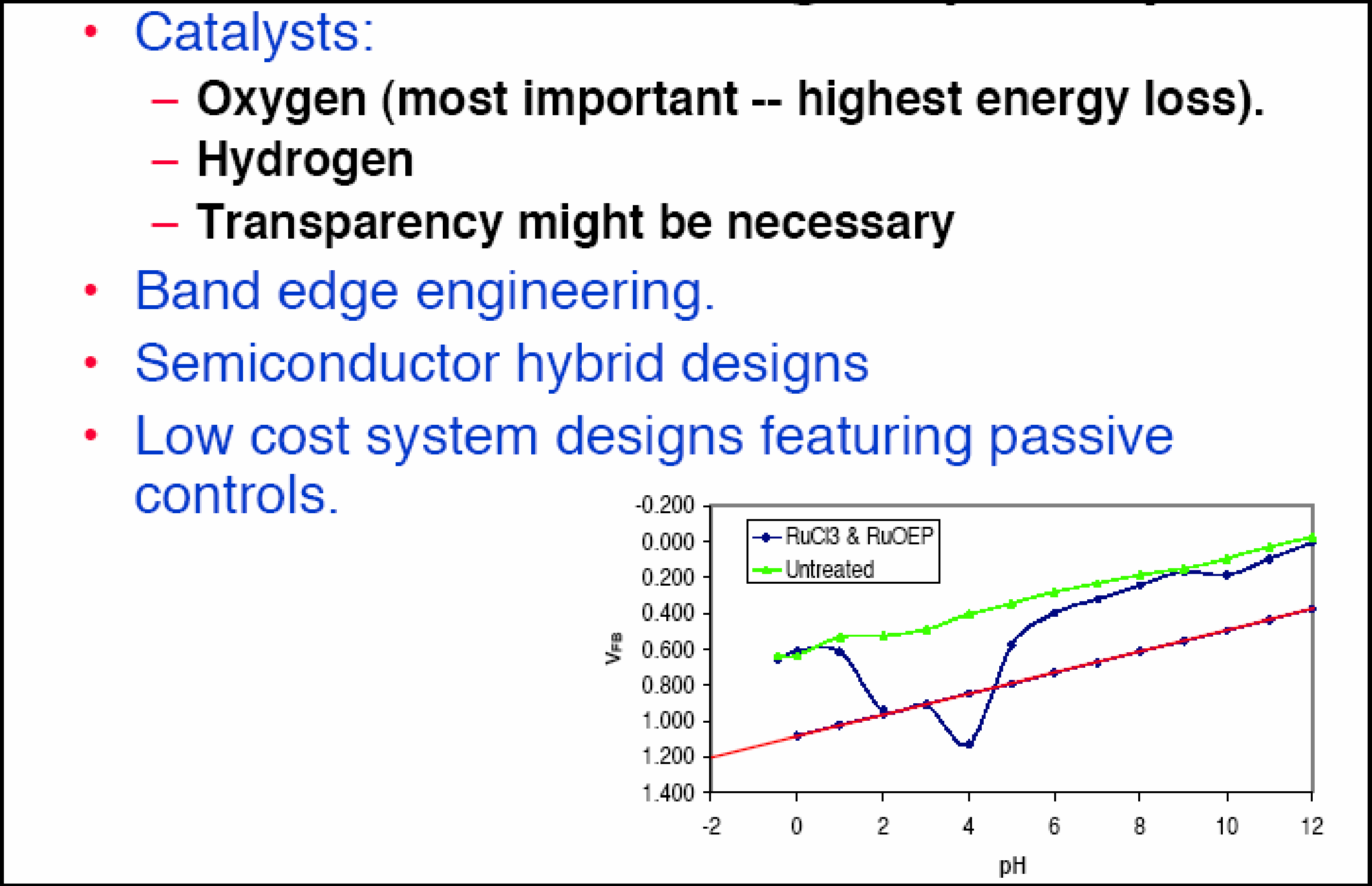
T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, International Journal of Hydrogen Energy 27 (2002) 991– 1022

Technical Challenges



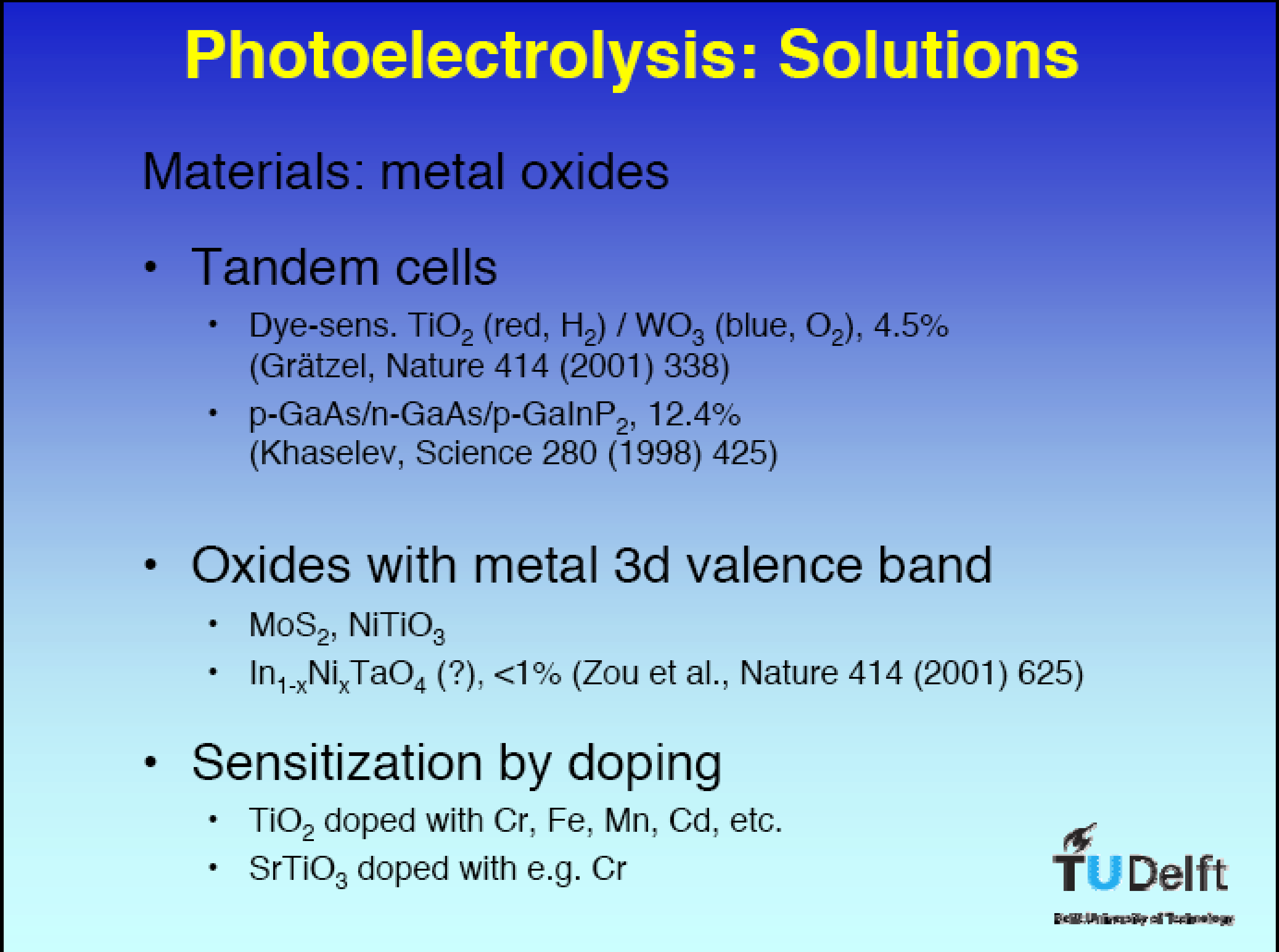
- Stability
  - The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.
- Efficiency (Bandgap)
  - For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with bandgaps in this range are photochemically unstable in water.
- Energetics
  - In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energies where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

Technical Challenges



- Catalysts:
  - Oxygen (most important -- highest energy loss).
  - Hydrogen
  - Transparency might be necessary
- Band edge engineering.
- Semiconductor hybrid designs
- Low cost system designs featuring passive controls.

Photoelectrolysis

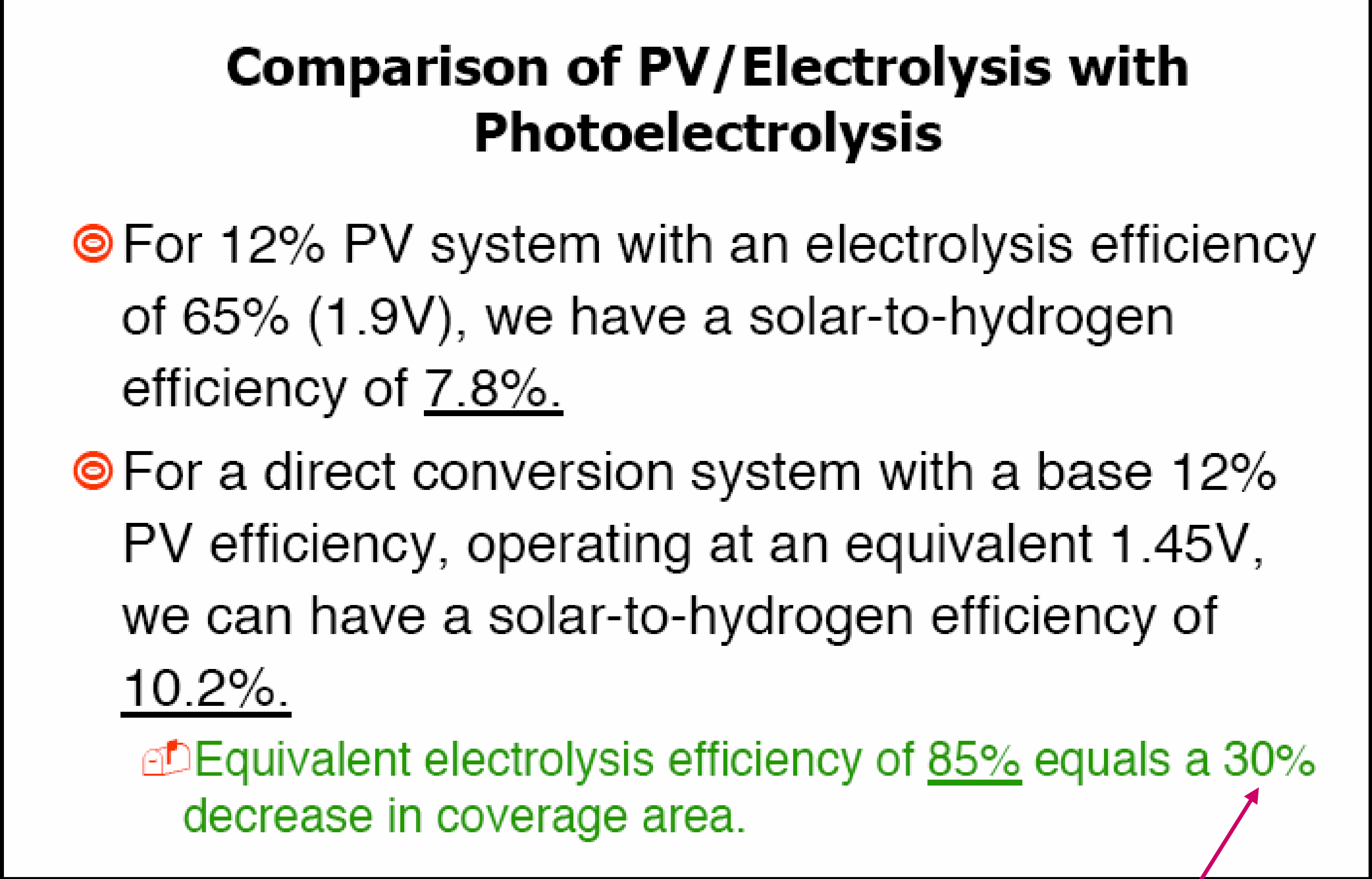


Photoelectrolysis: Solutions

Materials: metal oxides

- Tandem cells
  - Dye-sens. TiO_2 (red, H_2) / WO_3 (blue, O_2), 4.5% (Grätzel, Nature 414 (2001) 338)
  - p-GaAs/n-GaAs/p-GaInP_2, 12.4% (Khaselev, Science 280 (1998) 425)
- Oxides with metal 3d valence band
  - MoS_2, $NiTiO_3$
  - $In_{1-x}Ni_xTaO_4$ (?), <1% (Zou et al., Nature 414 (2001) 625)
- Sensitization by doping
  - TiO_2 doped with Cr, Fe, Mn, Cd, etc.
  - $SrTiO_3$ doped with e.g. Cr

Photoelectrolysis

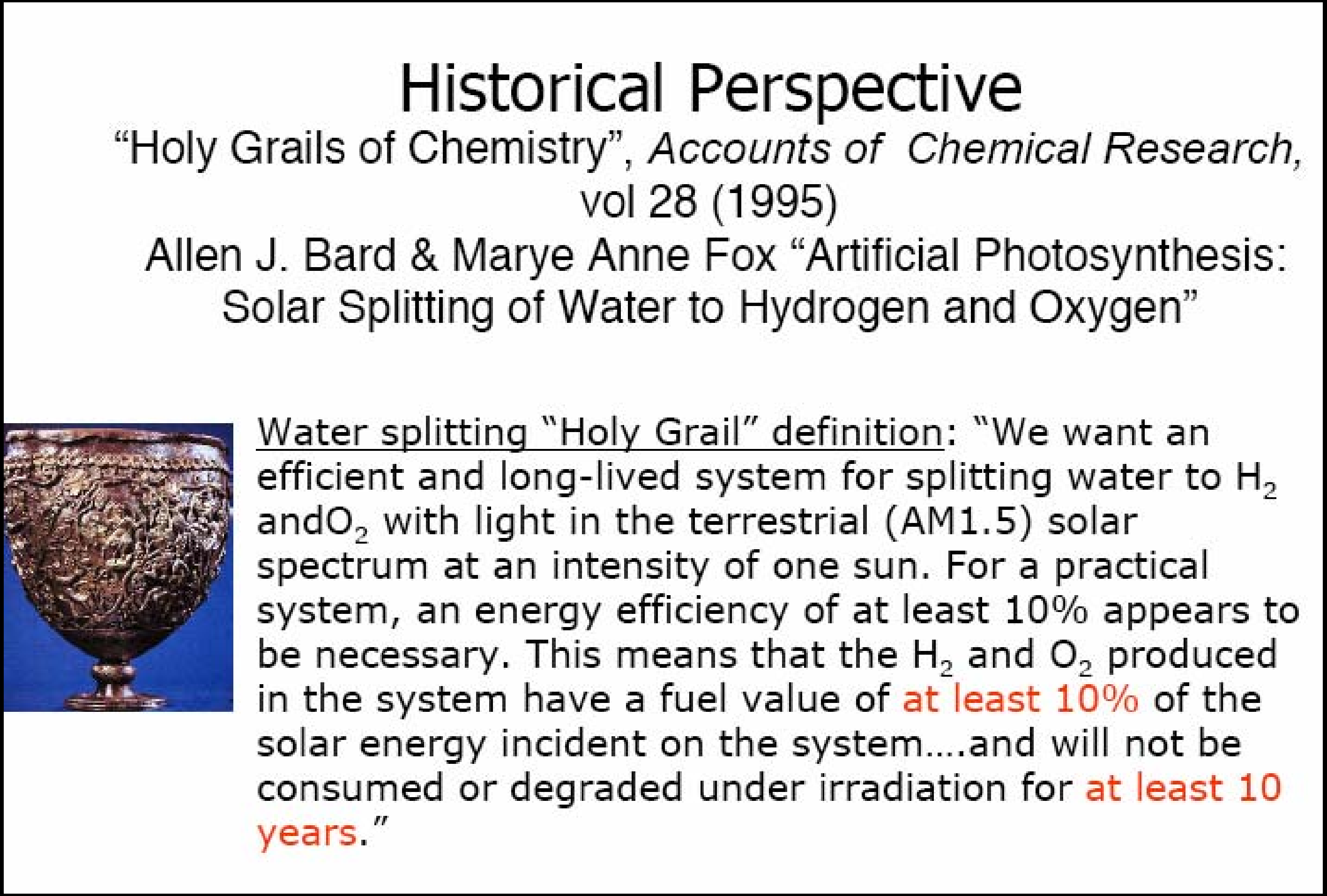


Comparison of PV/Electrolysis with Photoelectrolysis

- For 12% PV system with an electrolysis efficiency of 65% (1.9V), we have a solar-to-hydrogen efficiency of 7.8%.
- For a direct conversion system with a base 12% PV efficiency, operating at an equivalent 1.45V, we can have a solar-to-hydrogen efficiency of 10.2%.
  - Equivalent electrolysis efficiency of 85% equals a 30% decrease in coverage area.

A strong motivation for improved electrolysis process

Photoelectrolysis



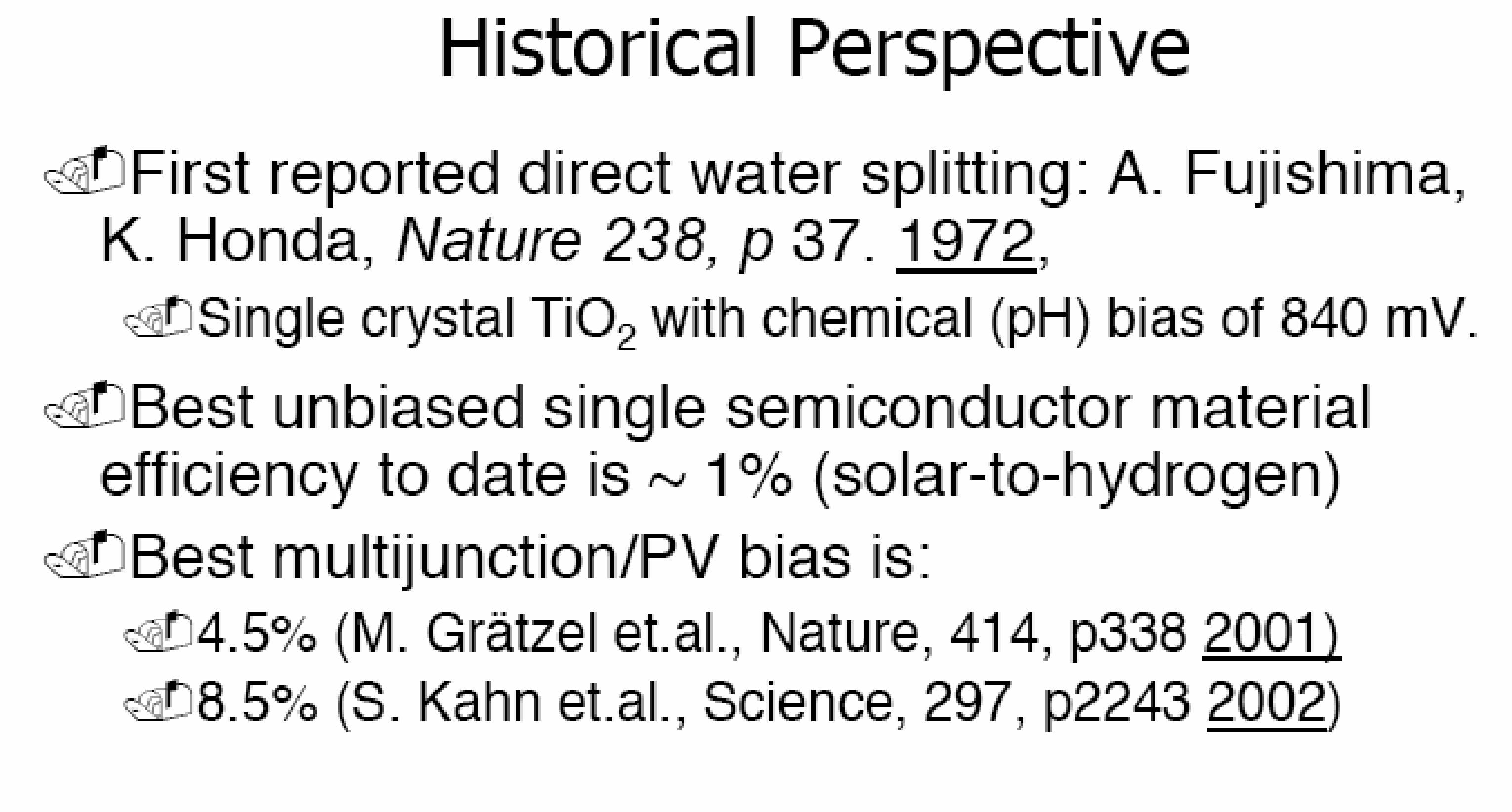
Historical Perspective

"Holy Grails of Chemistry", *Accounts of Chemical Research*, vol 28 (1995)

Allen J. Bard & Marye Anne Fox "Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen"

Water splitting "Holy Grail" definition: "We want an efficient and long-lived system for splitting water to H_2 andO_2 with light in the terrestrial (AM1.5) solar spectrum at an intensity of one sun. For a practical system, an energy efficiency of at least 10% appears to be necessary. This means that the H_2 and O_2 produced in the system have a fuel value of at least 10% of the solar energy incident on the system....and will not be consumed or degraded under irradiation for at least 10 years."

Photoelectrolysis

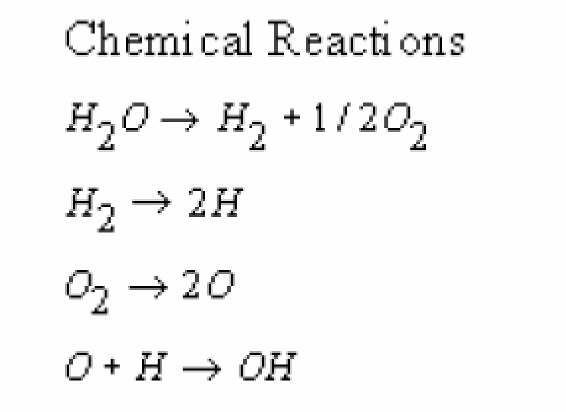


Historical Perspective

- First reported direct water splitting: A. Fujishima, K. Honda, *Nature 238, p* 37. 1972,
  - Single crystal TiO_2 with chemical (pH) bias of 840 mV.
- Best unbiased single semiconductor material efficiency to date is ~ 1% (solar-to-hydrogen)
- Best multijunction/PV bias is:
  - 4.5% (M. Grätzel et.al., Nature, 414, p338 2001)
  - 8.5% (S. Kahn et.al., Science, 297, p2243 2002)

Thermal Decomposition of Water

By heating water to over 2,000ºC, it is broken down into hydrogen and oxygen. This is considered to be an interesting and inexpensive method of producing hydrogen directly from solar energy. Research is also being done on the use of catalysts to reduce the temperature for dissociation. One central problem is the separation of gases at high temperatures to avoid recombining. The efficiency factor is uncertain.



Chemical Reactions

$H_2O \rightarrow H_2 + 1/2O_2$

$H_2 \rightarrow 2H$

$O_2 \rightarrow 2O$

$O + H \rightarrow OH$

Thermochemical Production from Nuclear Energy

Hydrogen can be produced from water using thermal energy

- Electric power generation → Electrolysis
  - Proven technology
  - Overall efficiency ~24% (LWR), ~36% (Hi T Reactors)

    (efficiency of electric power generation x efficiency of electrolysis)
- Heat → Thermochemical water-splitting
  - Net plant efficiencies of up to ~50%
  - Developing technology
- Electricity + Heat → High temperature electrolysis or Hybrid cycles

Source: Ken Schultz
General Atomics
San Diego, CA

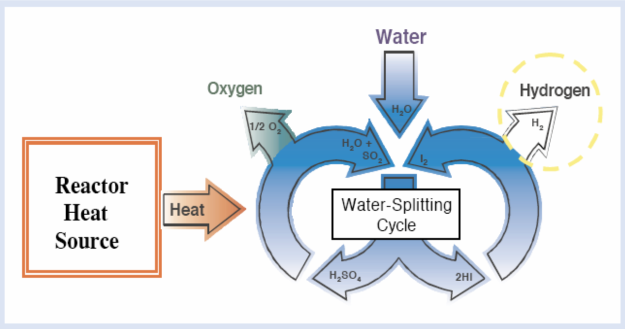
Thermochemical Production

- A set of coupled, thermally-driven chemical reactions that sum to the decomposition of water into H_2 and O_2
  - All reagents returned within the cycle and recycled
  - Only high temperature heat and water are input, only low temperature heat, H_2 and O_2 are output
- High efficiency is possible – at high temperature
- A developing technology
  - Explored extensively in the 1970s
  - Numerous possible cycles identified and explored
  - Never commercialized

Thermochemical Production

Identified the Sulfur-Iodine (S-I) as best suited for hydrogen production from a nuclear heat source

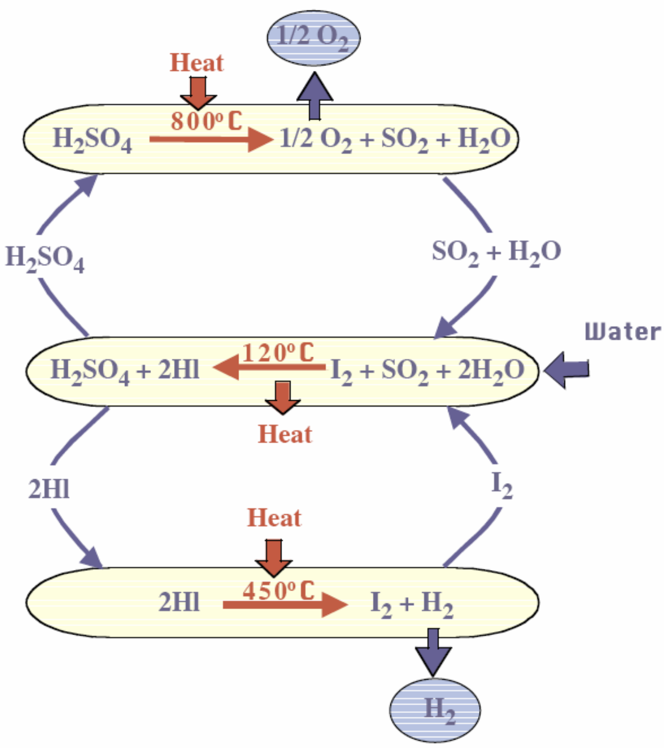
- Higher efficiency, easier handling
- France, Japan have also selected the S-I cycle (or "I-S cycle")



Ref.: Brown, *et al*, AIChE 2002

- **Invented at GA in 1970s**
  - Serious investigations for nuclear and solar
  - Chemistry reactions all demonstrated
  - Materials candidates selected and tested
- **Advantages:**
  - All fluid continuous process, chemicals all recycled; no effluents
  - H_2 produced at high pressure – 22 - 84 atm.
  - Highest cited projected efficiency, ~50%
- **Challenges:**
  - Requires high temperature, ≥800°C
  - Must be demonstrated as a closed loop under prototypical conditions

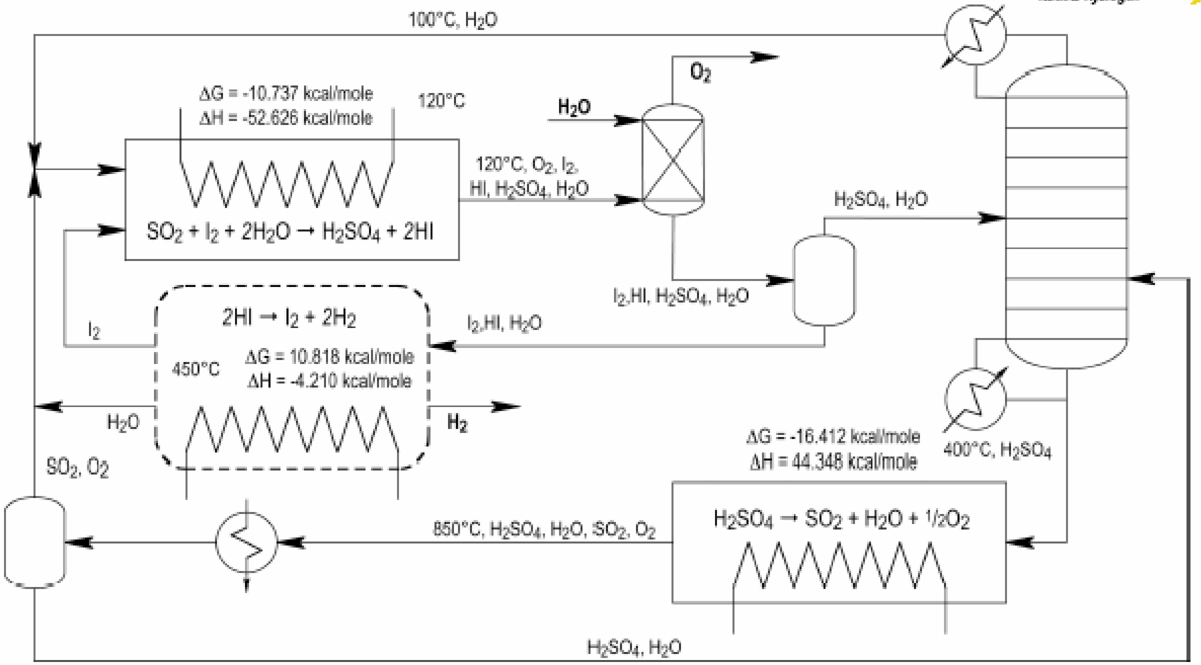
Sulfur-Iodine Thermochemical Water-Splitting Cycle



Thermochemical Production

The S-I cycle is a thermally-driven chemical process

NH2
Nuclear Hydrogen

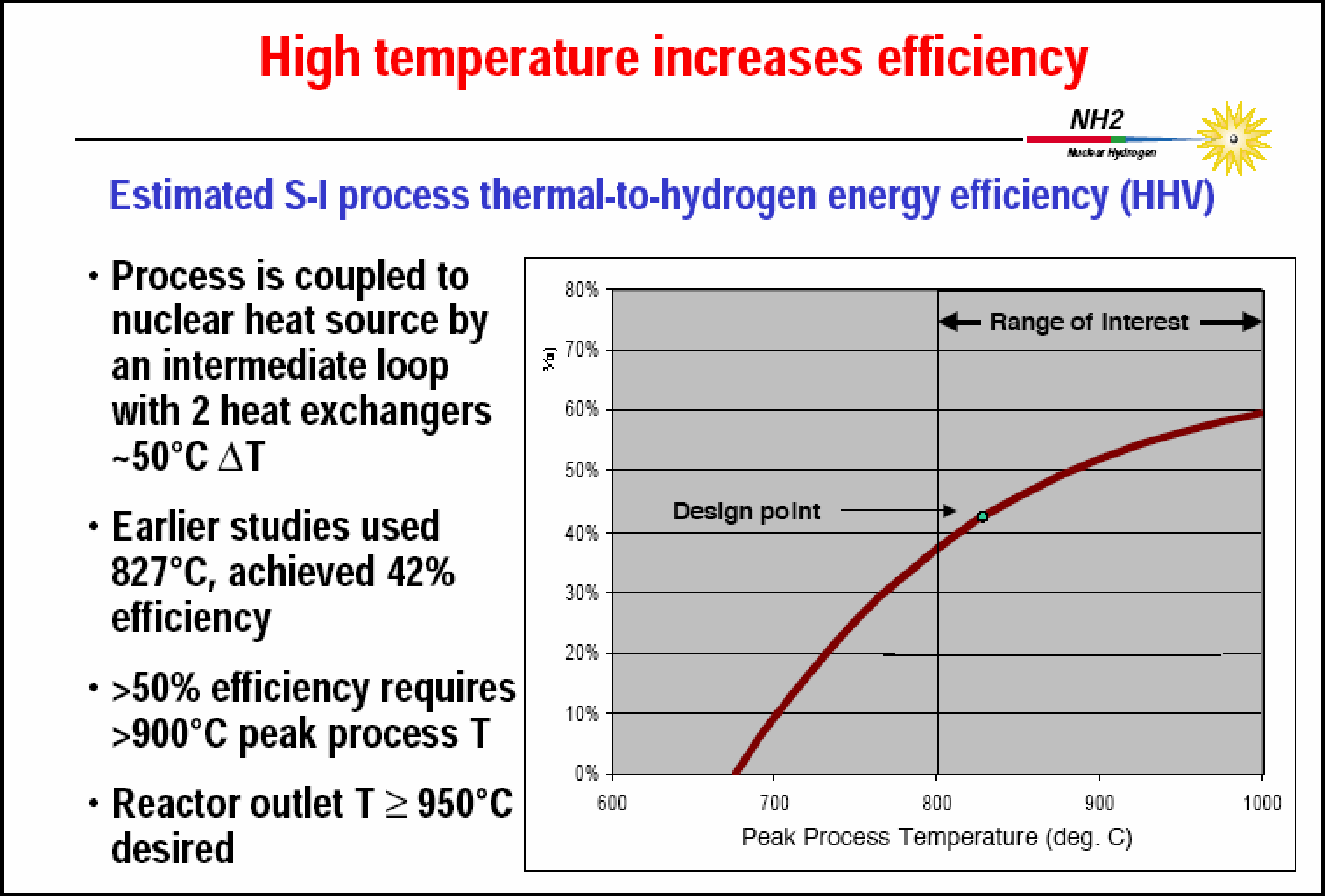


Follows the rules of chemistry and thermodynamics (Carnot)

High predicted efficiency: ~50% at 900°C

Thermochemical Production

Possible production of heat by solar thermal plant



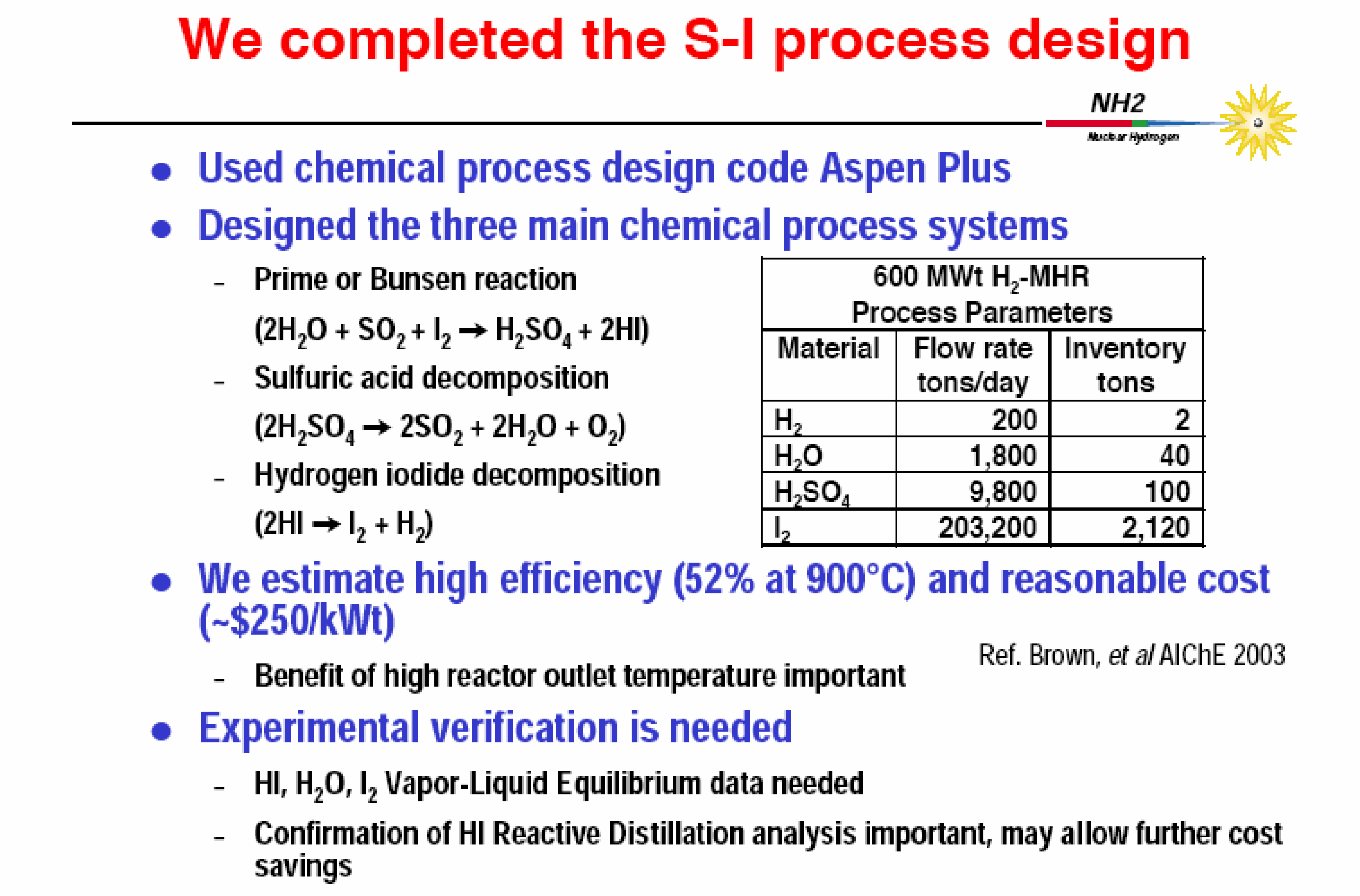
High temperature increases efficiency

NH2
Nuclear Hydrogen

Estimated S-I process thermal-to-hydrogen energy efficiency (HHV)

- Process is coupled to nuclear heat source by an intermediate loop with 2 heat exchangers ~50°C ΔT
- Earlier studies used 827°C, achieved 42% efficiency
- >50% efficiency requires >900°C peak process T
- Reactor outlet T ≥ 950°C desired

Thermochemical Production



We completed the S-I process design

NH2
Nuclear Hydrogen

- Used chemical process design code Aspen Plus
- Designed the three main chemical process systems
  - Prime or Bunsen reaction
    ($2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$)
  - Sulfuric acid decomposition
    ($2H_2SO_4 \rightarrow 2SO_2 + 2H_2O + O_2$)
  - Hydrogen iodide decomposition
    ($2HI \rightarrow I_2 + H_2$)

600 MWt H_2-MHR Process Parameters

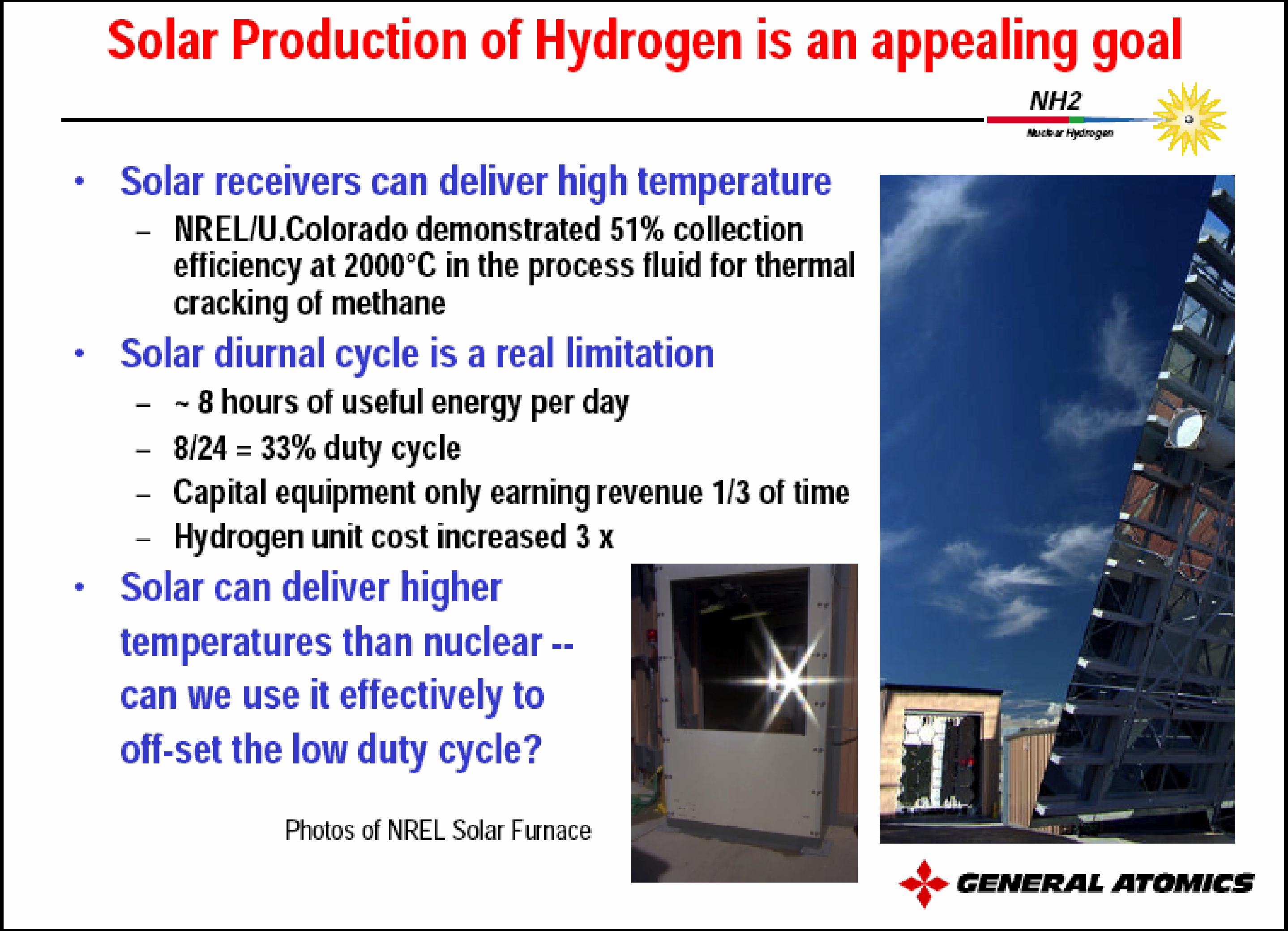
Material	Flow rate tons/day	Inventory tons
H_2	200	2
H_2O	1,800	40
H_2SO_4	9,800	100
I_2	203,200	2,120

- We estimate high efficiency (52% at 900°C) and reasonable cost (~$250/kWt)
  - Benefit of high reactor outlet temperature important

Ref. Brown, *et al* AIChE 2003

- Experimental verification is needed
  - HI, H_2O, I_2 Vapor-Liquid Equilibrium data needed
  - Confirmation of HI Reactive Distillation analysis important, may allow further cost savings

Thermochemical Production



Solar Production of Hydrogen is an appealing goal

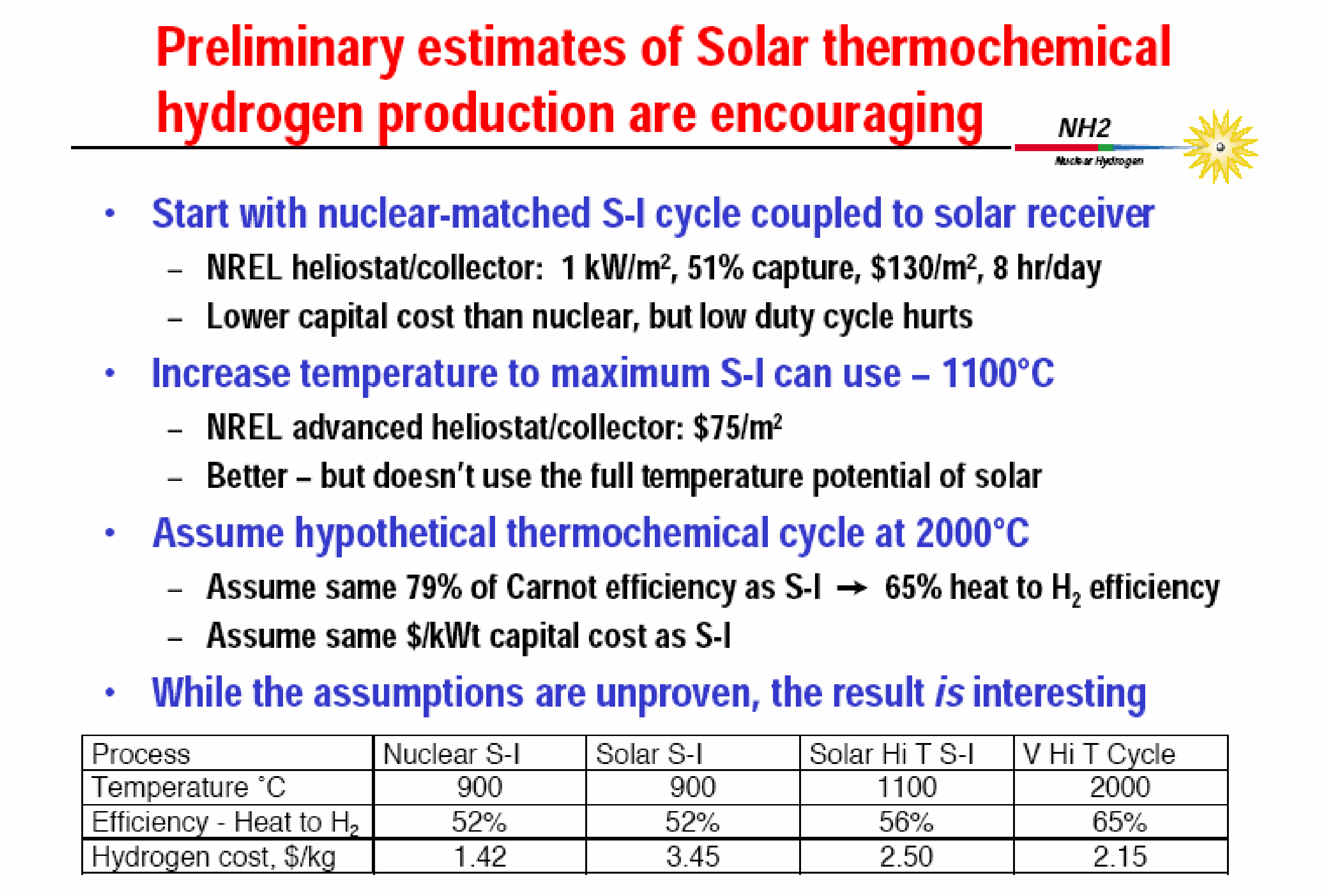
NH2
Nuclear Hydrogen

- Solar receivers can deliver high temperature
  - NREL/U.Colorado demonstrated 51% collection efficiency at 2000°C in the process fluid for thermal cracking of methane
- Solar diurnal cycle is a real limitation
  - ~ 8 hours of useful energy per day
  - 8/24 = 33% duty cycle
  - Capital equipment only earning revenue 1/3 of time
  - Hydrogen unit cost increased 3 x
- Solar can deliver higher temperatures than nuclear -- can we use it effectively to off-set the low duty cycle?

Photos of NREL Solar Furnace

GENERAL ATOMICS

Thermochemical Production



Preliminary estimates of Solar thermochemical hydrogen production are encouraging

- Start with nuclear-matched S-I cycle coupled to solar receiver
  - NREL heliostat/collector: 1 kW/m^2, 51% capture, \$130/m^2, 8 hr/day
  - Lower capital cost than nuclear, but low duty cycle hurts
- Increase temperature to maximum S-I can use – 1100°C
  - NREL advanced heliostat/collector: \$75/m^2
  - Better – but doesn't use the full temperature potential of solar
- Assume hypothetical thermochemical cycle at 2000°C
  - Assume same 79% of Carnot efficiency as S-I → 65% heat to H_2 efficiency
  - Assume same \$/kWt capital cost as S-I
- While the assumptions are unproven, the result *is* interesting

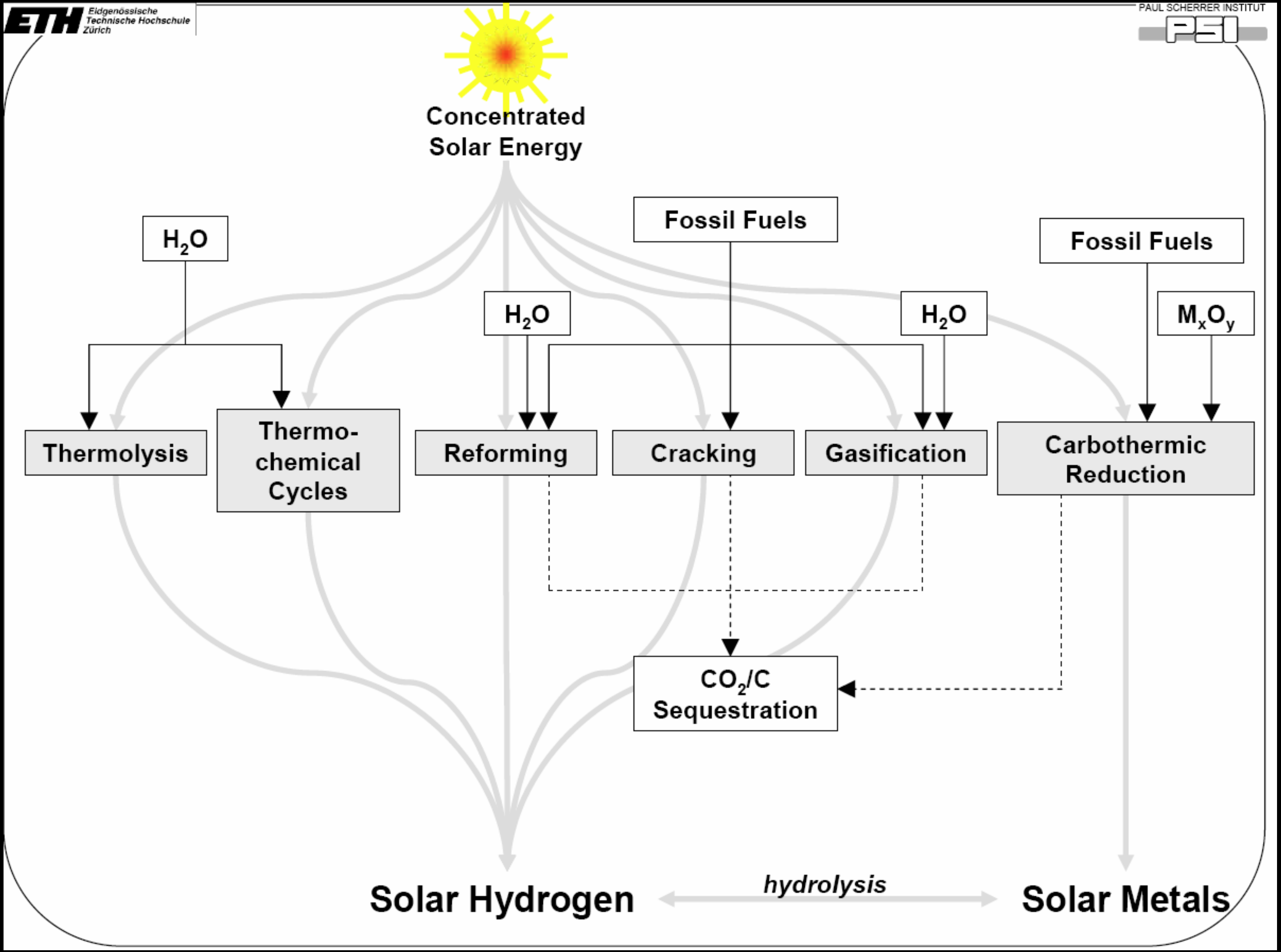
Process	Nuclear S-I	Solar S-I	Solar Hi T S-I	V Hi T Cycle
Temperature ˚C	900	900	1100	2000
Efficiency - Heat to H_2	52%	52%	56%	65%
Hydrogen cost, \$/kg	1.42	3.45	2.50	2.15

Hydrogen From Water

	Process Temperature (°C)	Heat-to-Hydrogen Efficiency (%)	Status
Electrolysis		20-25	Commercial
Sulfur-iodine thermochemical cycle	850	45-49	Pre-pilot
Calcium-bromine thermochemical cycle	760	36-40	Pilot plant
Copper-chlorine thermochemical cycle	550	41*	R&D-ANL

* Energy efficiency calculated based on thermodynamics

Solar Thermochemical Production



Concentrated Solar Energy

H_2O

Fossil Fuels

Fossil Fuels

H_2O

H_2O

M_xO_y

Thermolysis

Thermo-chemical Cycles

Reforming

Cracking

Gasification

Carbothermic Reduction

CO_2/C Sequestration

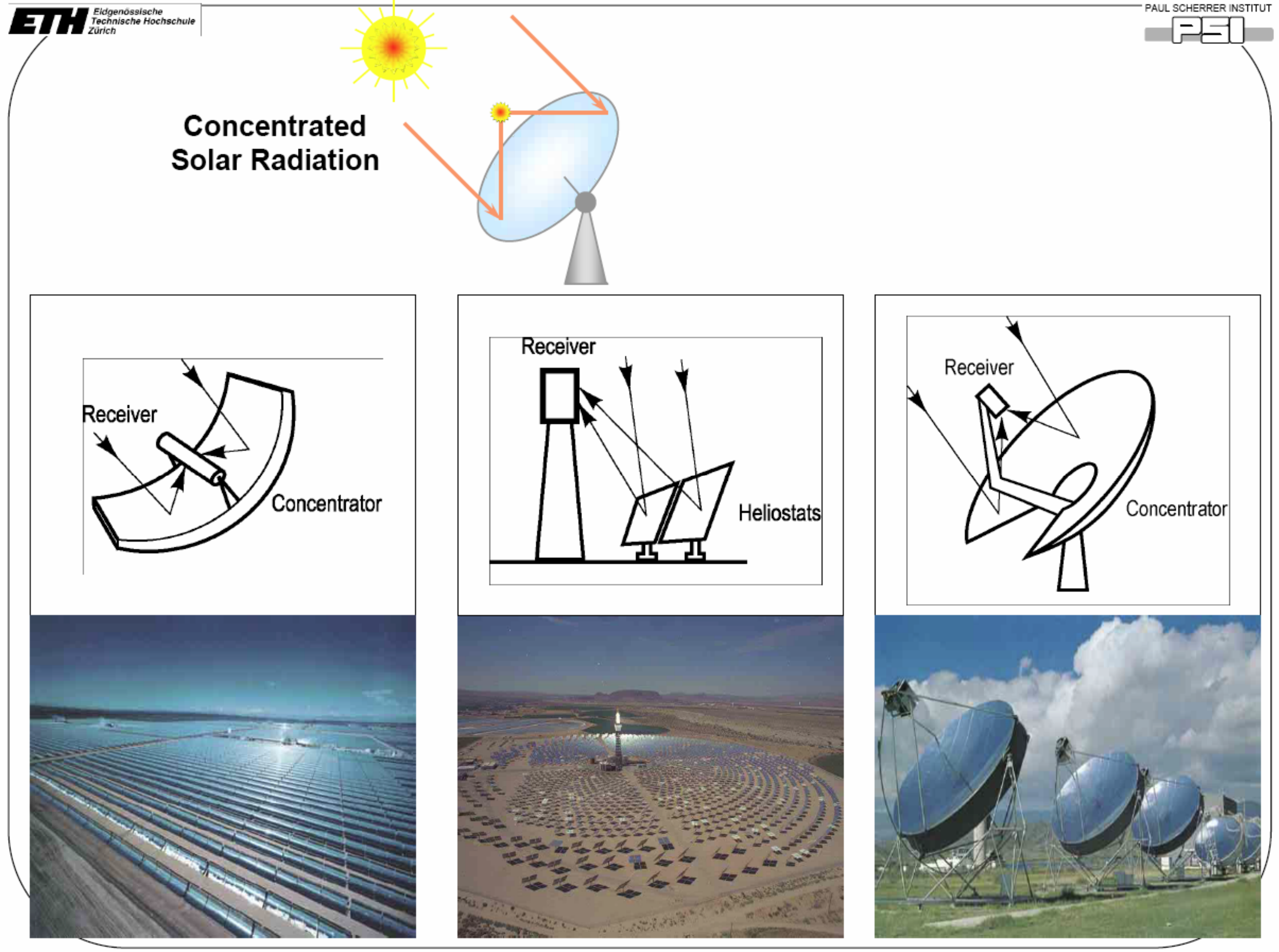
Solar Hydrogen

hydrolysis

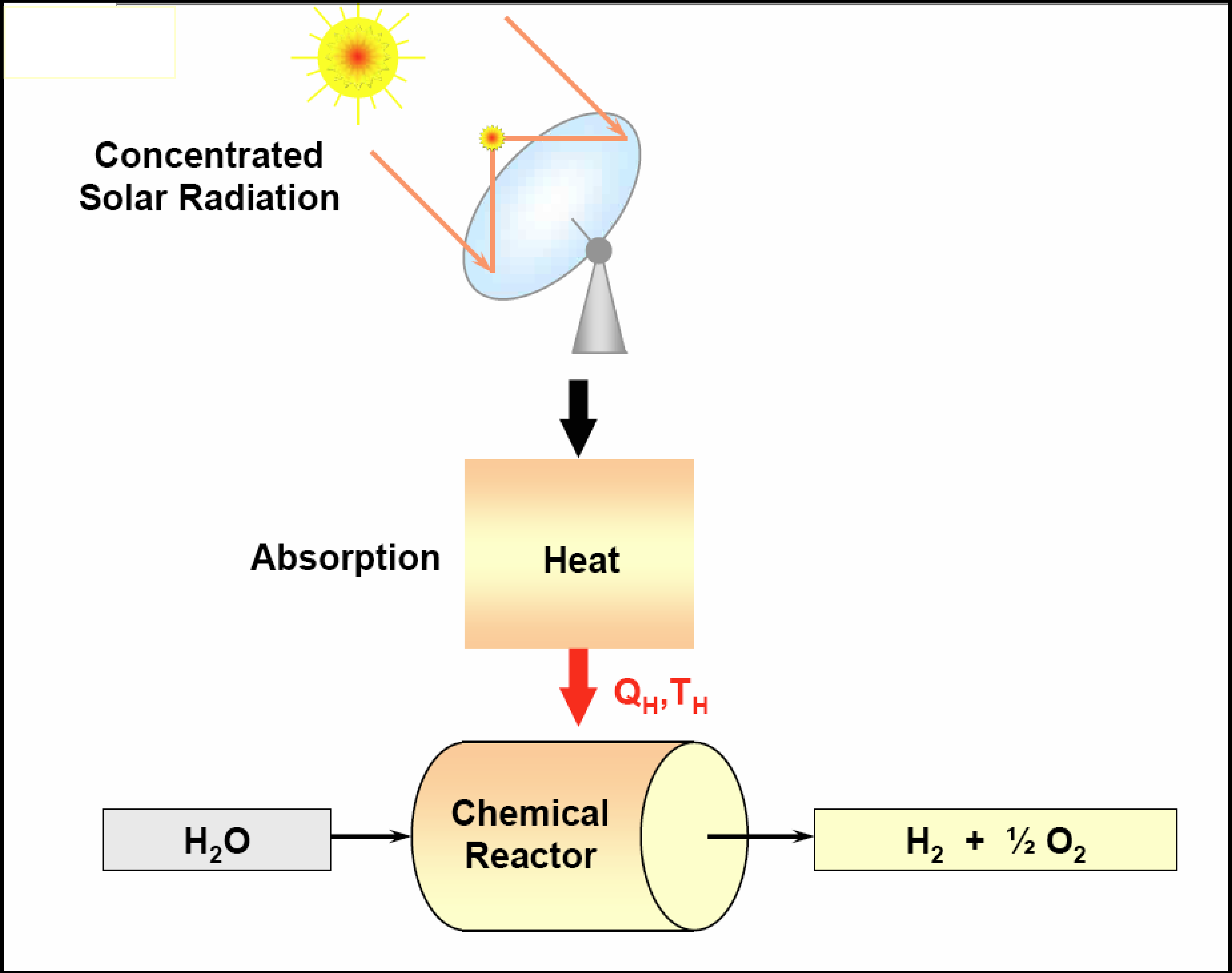
Solar Metals

Source: Aldo Steinfeld

Solar Thermochemical Production



Solar Thermochemical Production



Concentrated Solar Radiation

Absorption

Heat

Q_H, T_H

H_2O → Chemical Reactor → $H_2 + \frac{1}{2} O_2$

Copper-Chlorine Cycle

Hydrogen Production (160^{o}C)
$2Ag + 2HCl \rightarrow \mathbf{H_2(g)} + 2AgCl$

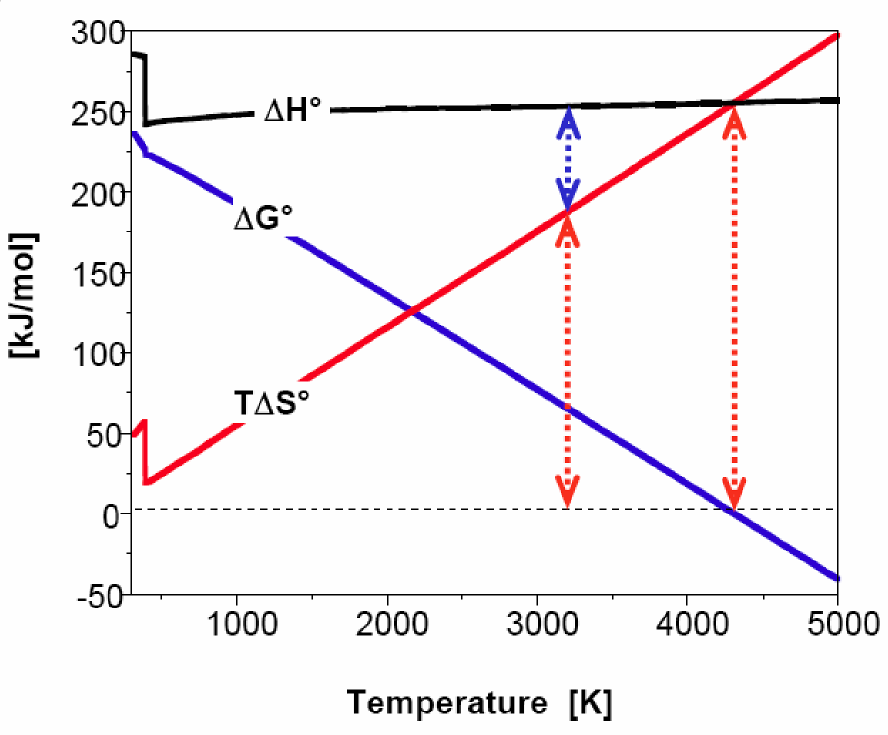
Intermediate Reaction (40^{o}C)
$2AgCl + 2CuCl + 8NH_3(g) \rightarrow 2Ag + 2CuCl_2 + 8NH_3(a)$
The reaction takes place in an aqueous media.

Oxygen Formation (550^{o}C)
$2CuCl_2 + 2MgO + \mathbf{H_2O} \rightarrow \mathbf{1/2O_2(g)} + 2HCl + 2CuCl + 2MgO$
Reaction consists of a complex set of reactions in which MgO is chlorinated to $MgCl_2$ Åú H_2O at 270^{o}C and transformed back into MgO at 550^{o}C.

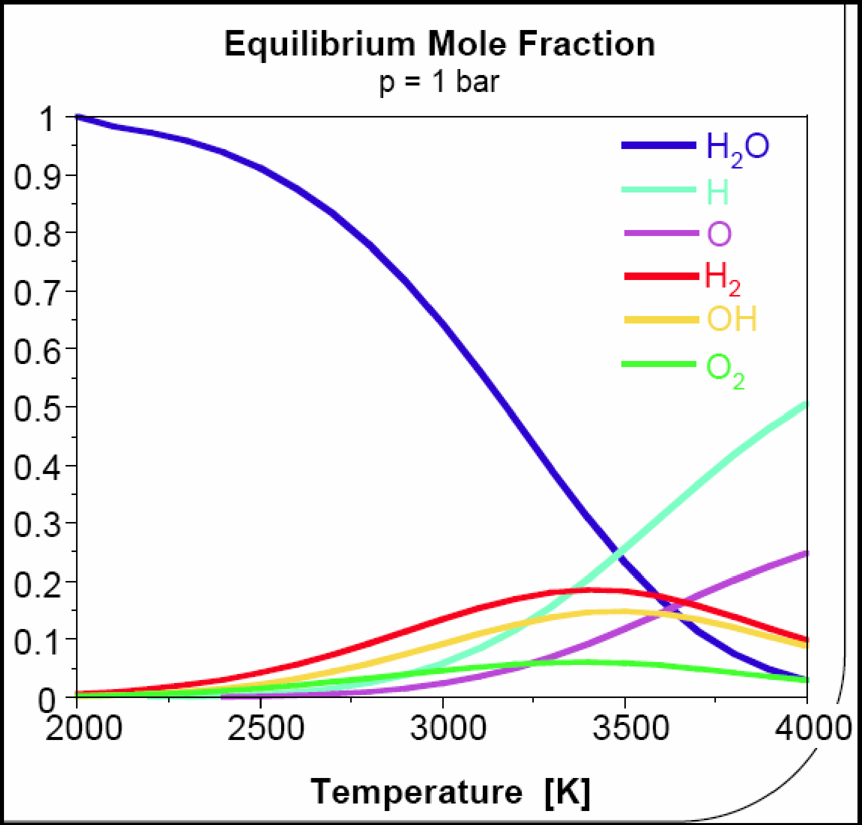
Net Reaction: $\mathbf{H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)}$

*Lecart, B., et al., *Int. J. Hydrogen Energy*, Vol. 4, pp. 7-11, **1979**.

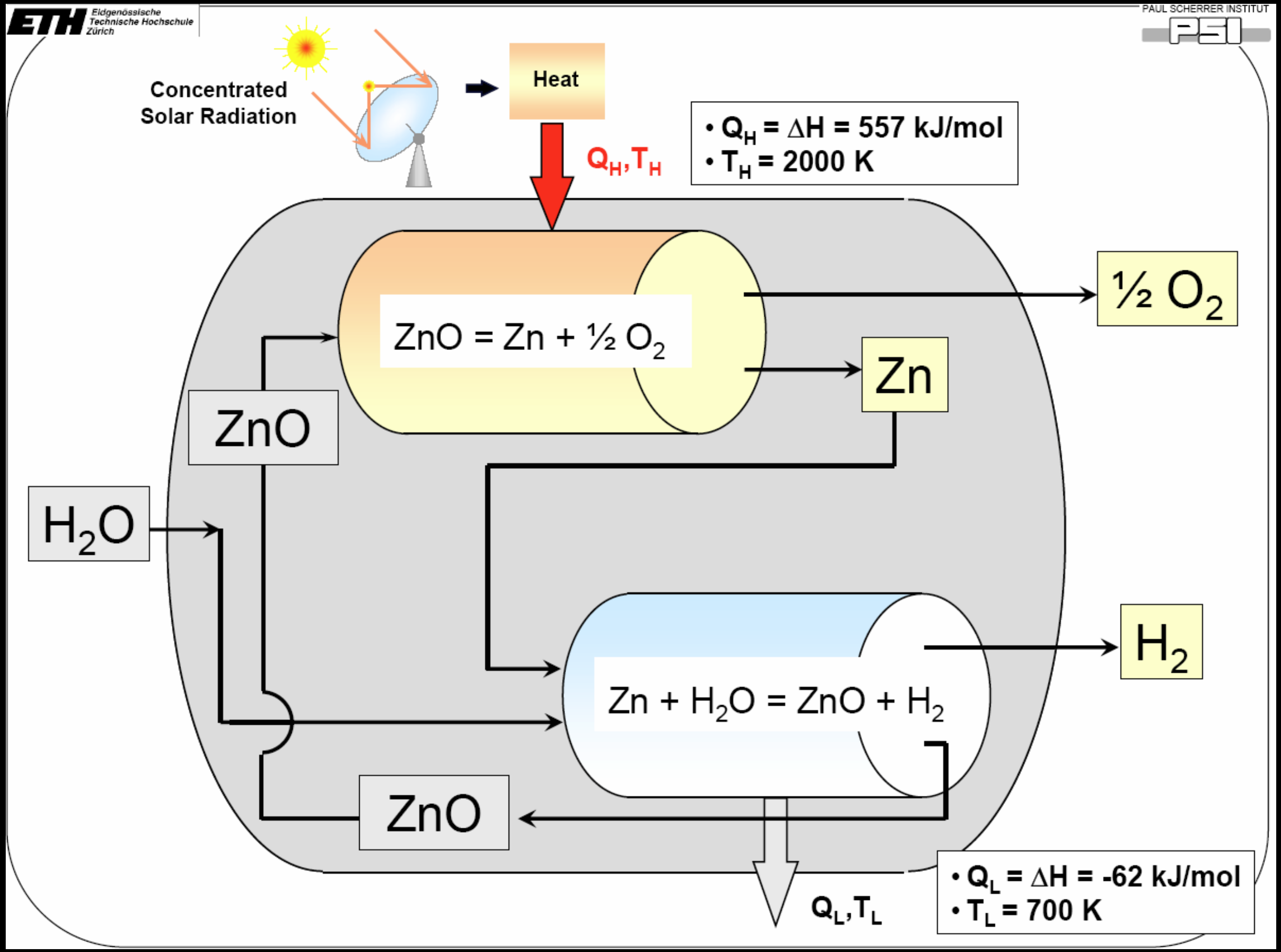
Solar Thermochemical Production



$$H_2O = H_2 + \frac{1}{2}O_2$$

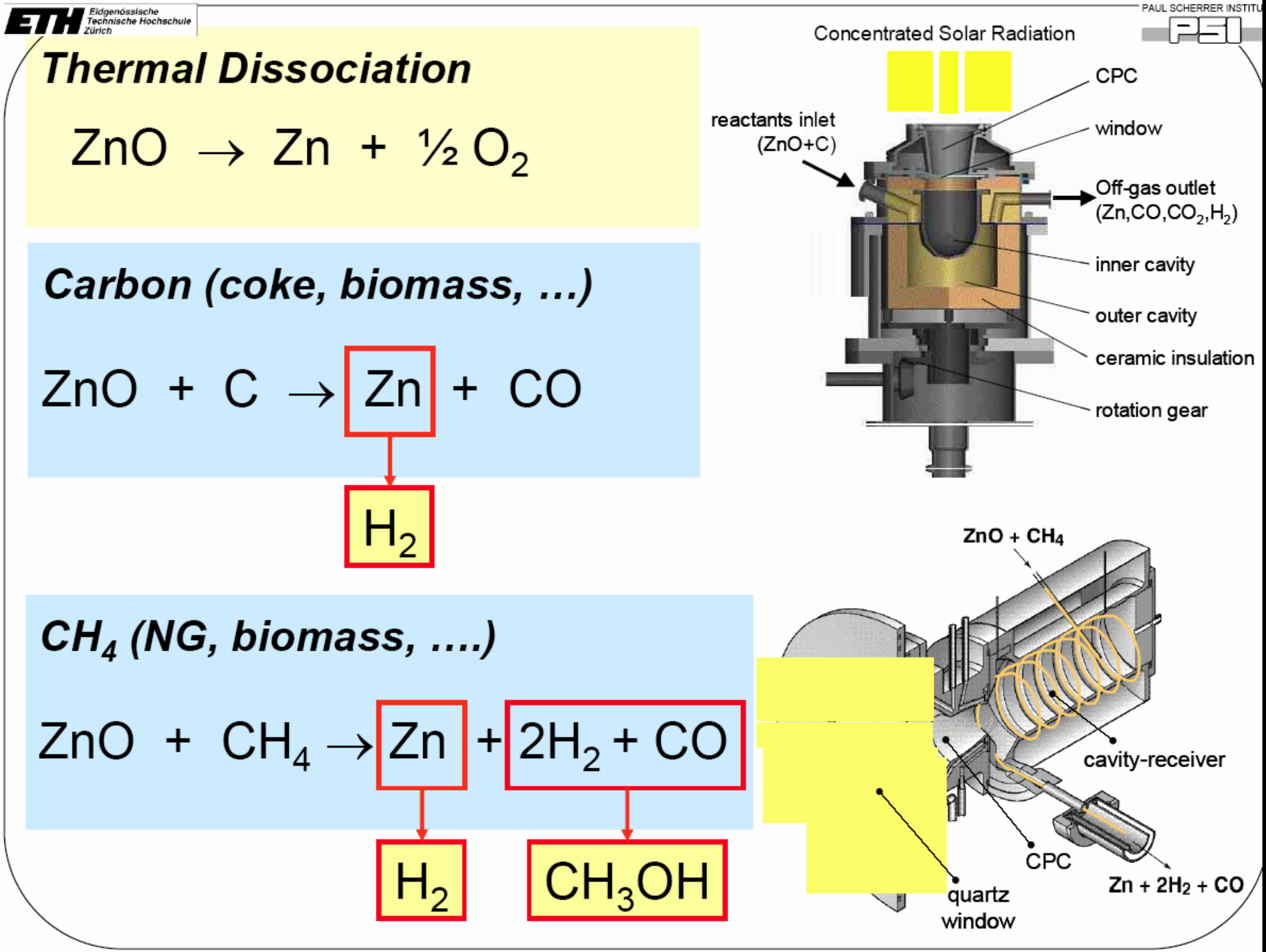


ZnO Disassociation



ZnO serves the functions of radiant absorber, thermal insulator, and chemical reactant.

ZnO Disassociation



ETH Eidgenössische Technische Hochschule Zürich

PAUL SCHERRER INSTITUT PSI

Thermal Dissociation

$$ZnO \rightarrow Zn + \frac{1}{2} O_2$$

Carbon (coke, biomass, ...)

$$ZnO + C \rightarrow \boxed{Zn} + CO$$

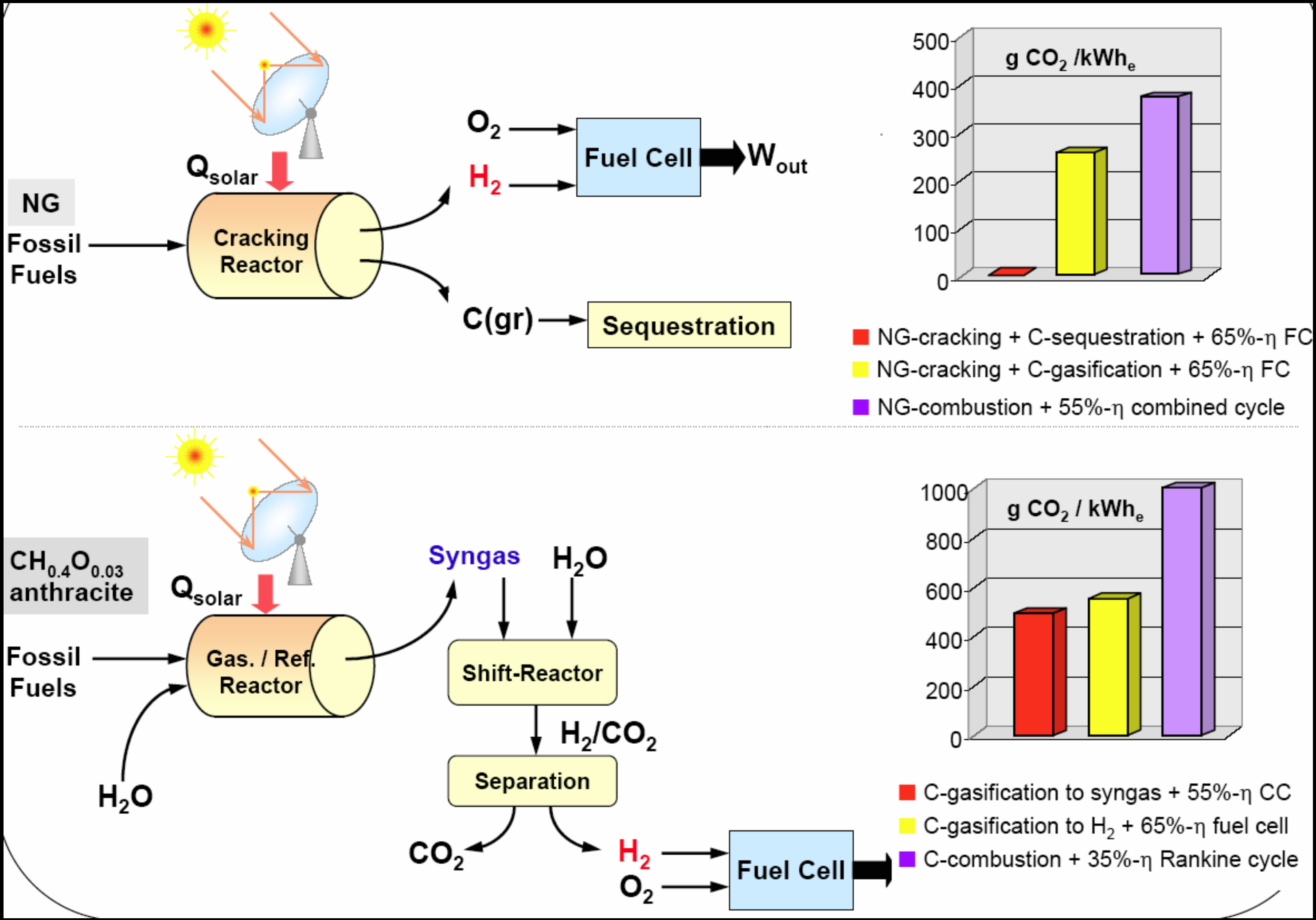
$$\boxed{Zn} \rightarrow \boxed{H_2}$$

CH_4 (NG, biomass, ...)

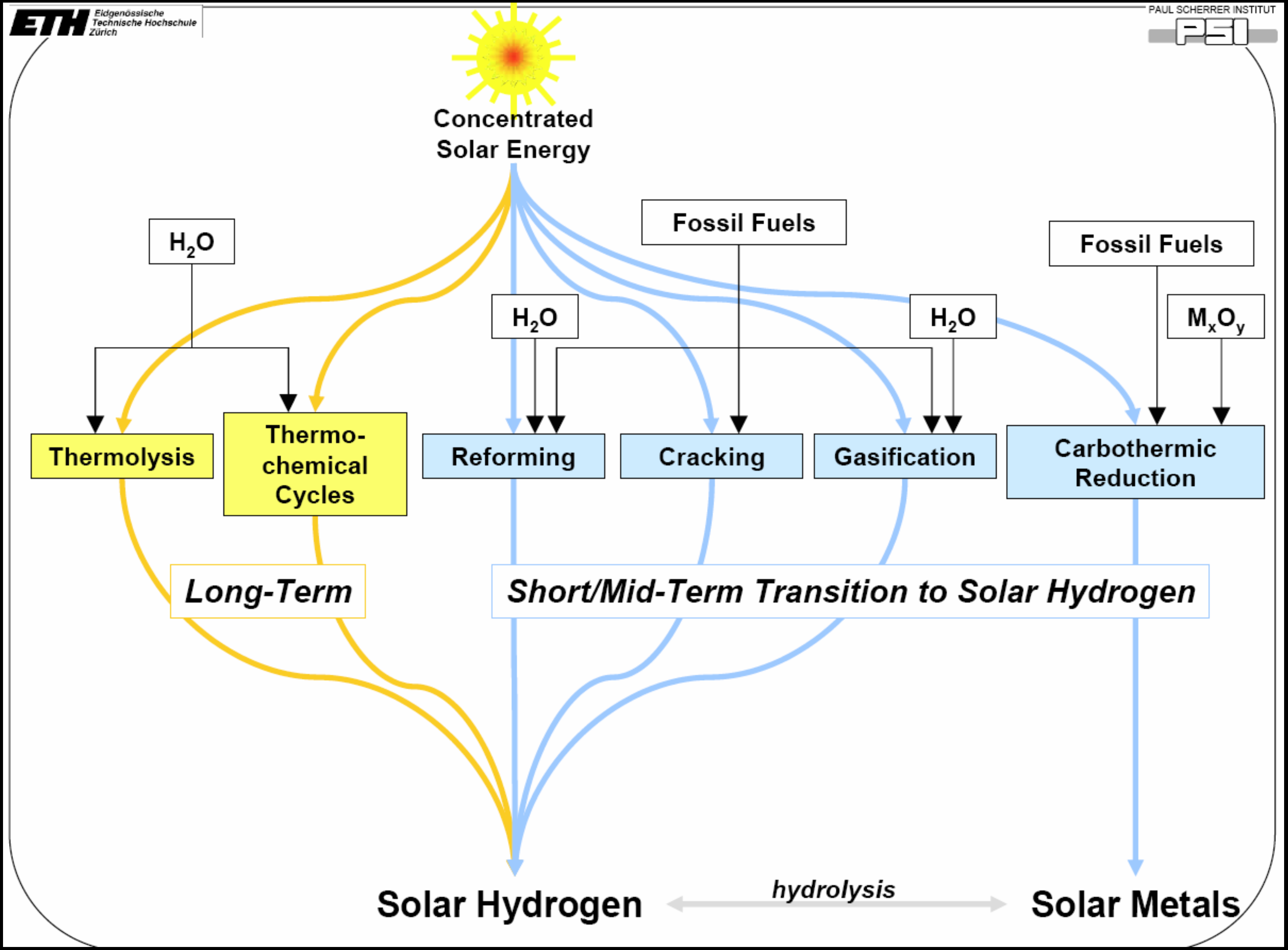
$$ZnO + CH_4 \rightarrow \boxed{Zn} + \boxed{2H_2 + CO}$$

$$\boxed{Zn} \rightarrow \boxed{H_2} \qquad \boxed{2H_2 + CO} \rightarrow \boxed{CH_3OH}$$

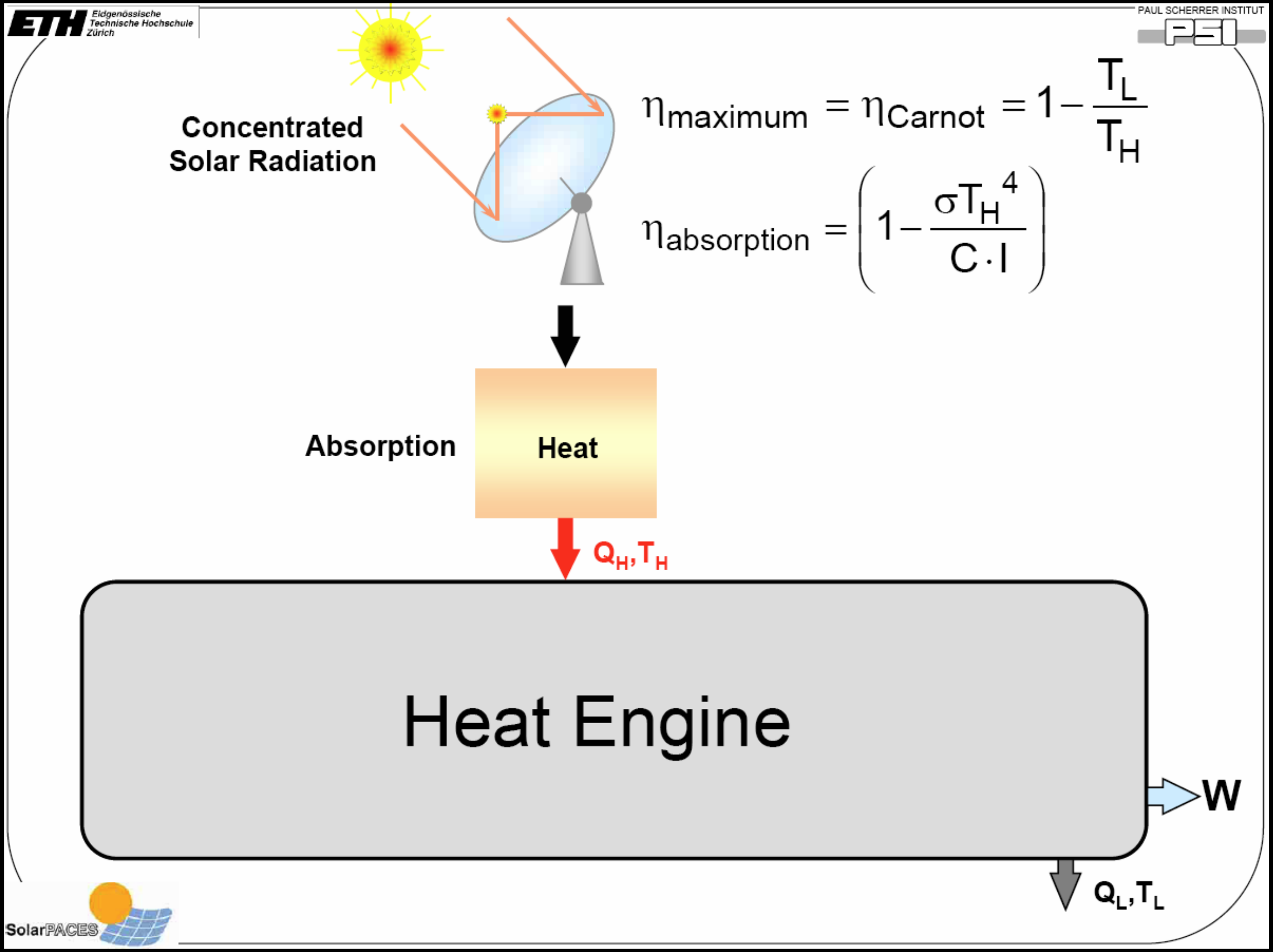
Decarbonization of Fossil Fuels



Timeline


Eidgenössische Technische Hochschule Zürich
PAUL SCHERRER INSTITUT
Concentrated Solar Energy
H_2O
Fossil Fuels
Fossil Fuels
H_2O
H_2O
M_xO_y
Thermolysis
Thermo-chemical Cycles
Reforming
Cracking
Gasification
Carbothermic Reduction
Long-Term
Short/Mid-Term Transition to Solar Hydrogen
Solar Hydrogen
hydrolysis
Solar Metals

Efficiency



Concentrated Solar Radiation

$$\eta_{maximum} = \eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

$$\eta_{absorption} = \left(1 - \frac{\sigma T_H^{\ 4}}{C \cdot I}\right)$$

Absorption

Heat

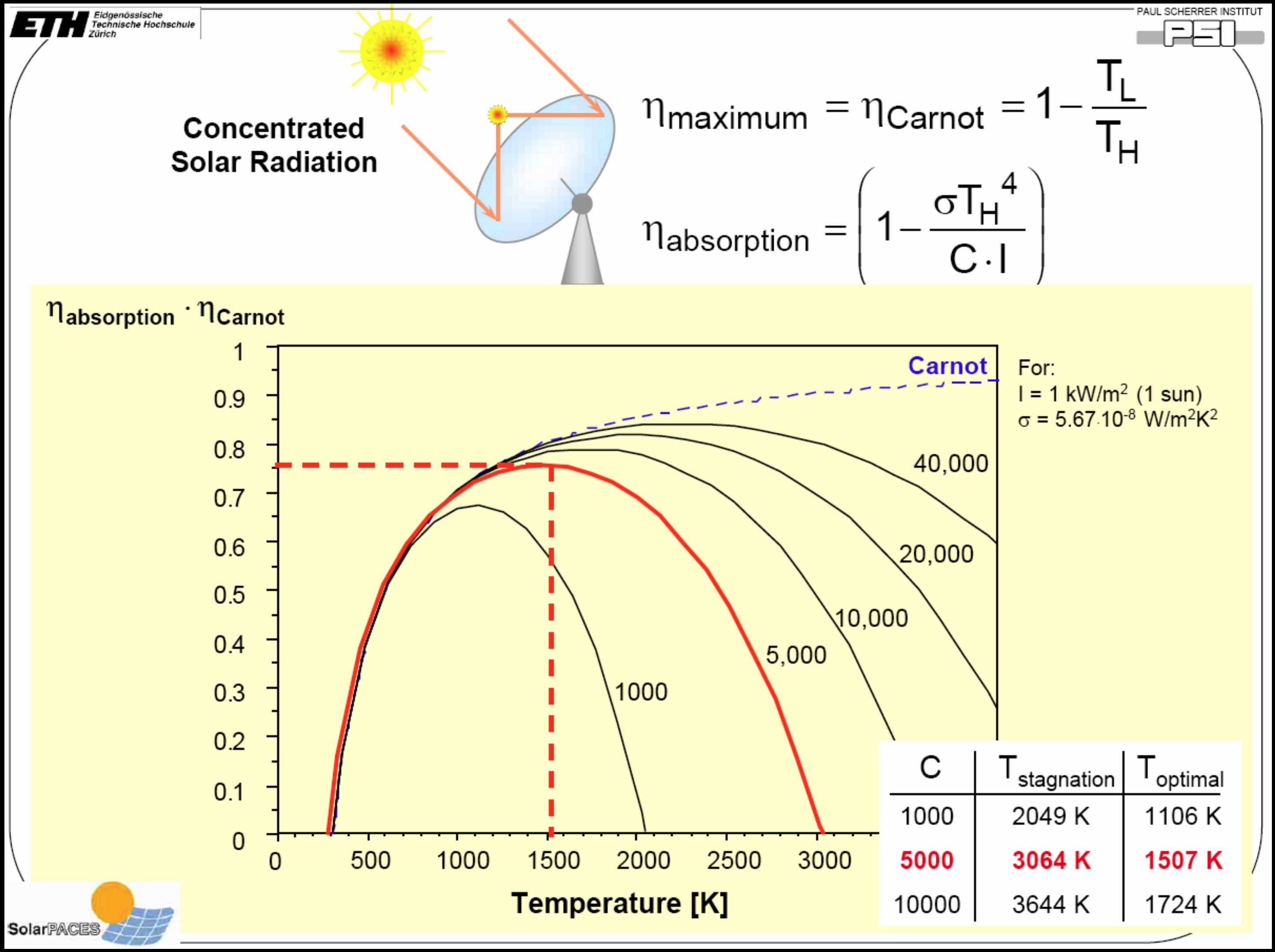
Q_H, T_H

Heat Engine

W

Q_L, T_L

Efficiency



Concentrated Solar Radiation

$$\eta_{\text{maximum}} = \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}$$

$$\eta_{\text{absorption}} = \left(1 - \frac{\sigma T_H^4}{C \cdot I}\right)$$

$\eta_{\text{absorption}} \cdot \eta_{\text{Carnot}}$

Temperature [K]

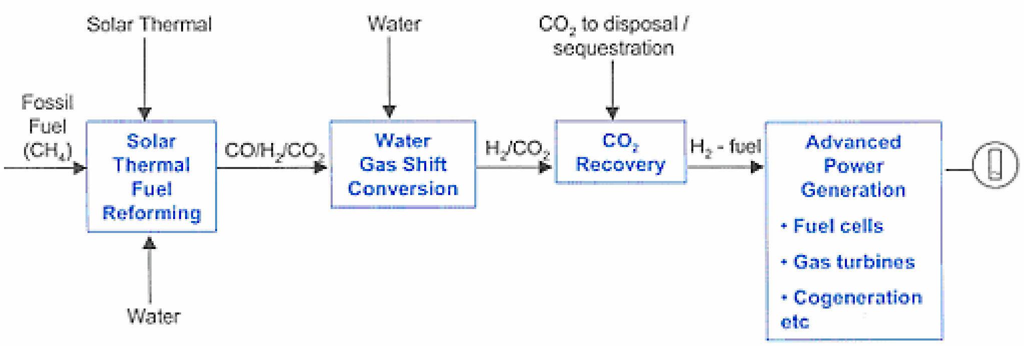
For:
$I = 1\ \text{kW/m}^2$ (1 sun)
$\sigma = 5.67 \cdot 10^{-8}\ \text{W/m}^2\text{K}^2$

C	$T_{\text{stagnation}}$	T_{optimal}
1000	2049 K	1106 K
5000	3064 K	1507 K
10000	3644 K	1724 K

Solar Thermal Project

CSIRO in collaboration with industry partner Solar Systems Pty Ltd has demonstrated a concept for integrating solar thermal energy and methane gas to produce a range of solar-enriched fuels and synthesis gas (CO and H_2) that can be used as a power generation fuel gas, as a metallurgical reducing gas or as chemical feed stock e.g. in methanol production.

The main chemical processes are:



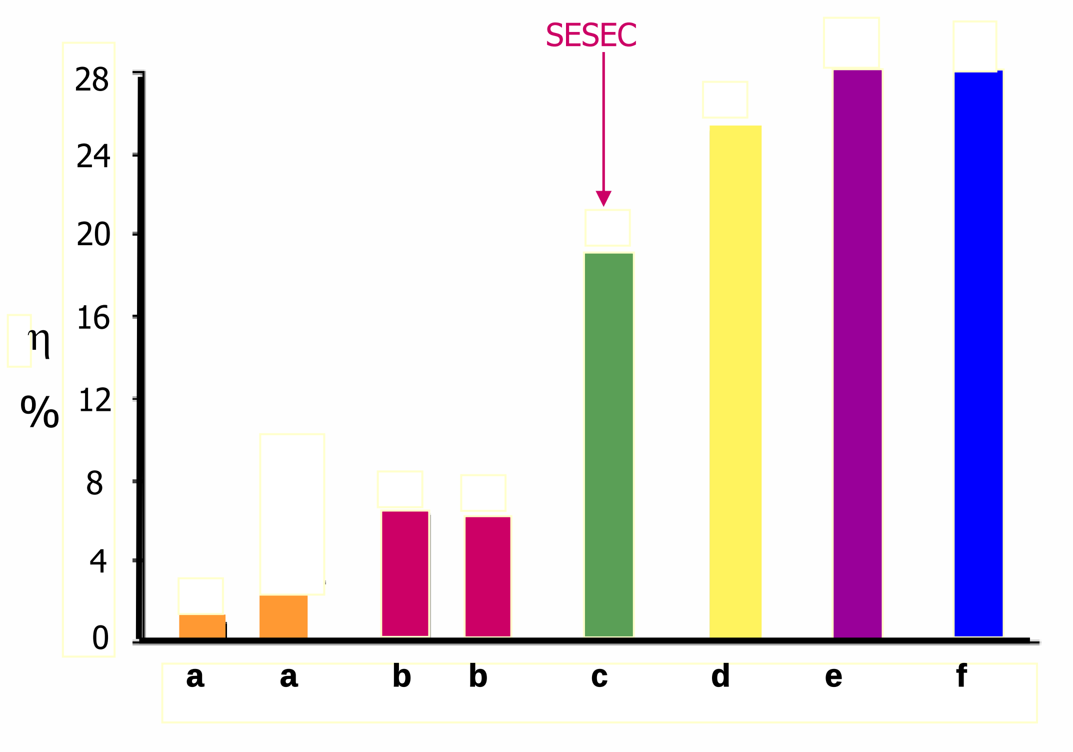
$CH_4 + H_2O_{(L)} + 250\ kJ \rightarrow CO + 3H_2$ (Reaction 1)

$CO + H_2O_{(L)} \rightarrow CO_2 + H_2 + 3\ kJ$ (Reaction 2)

$CO + H_2O(l) \rightarrow H_2 + CO_2 + 3\ kJ$

http://www.energy.csiro.au/

Solar to Hydrogen Conversion Efficiency



a: Direct thermal hydrogen

b: Silicon photovoltaic cells and alkaline electrolyzer

c: Solar dish Stirling generator and alkaline electrolyzer

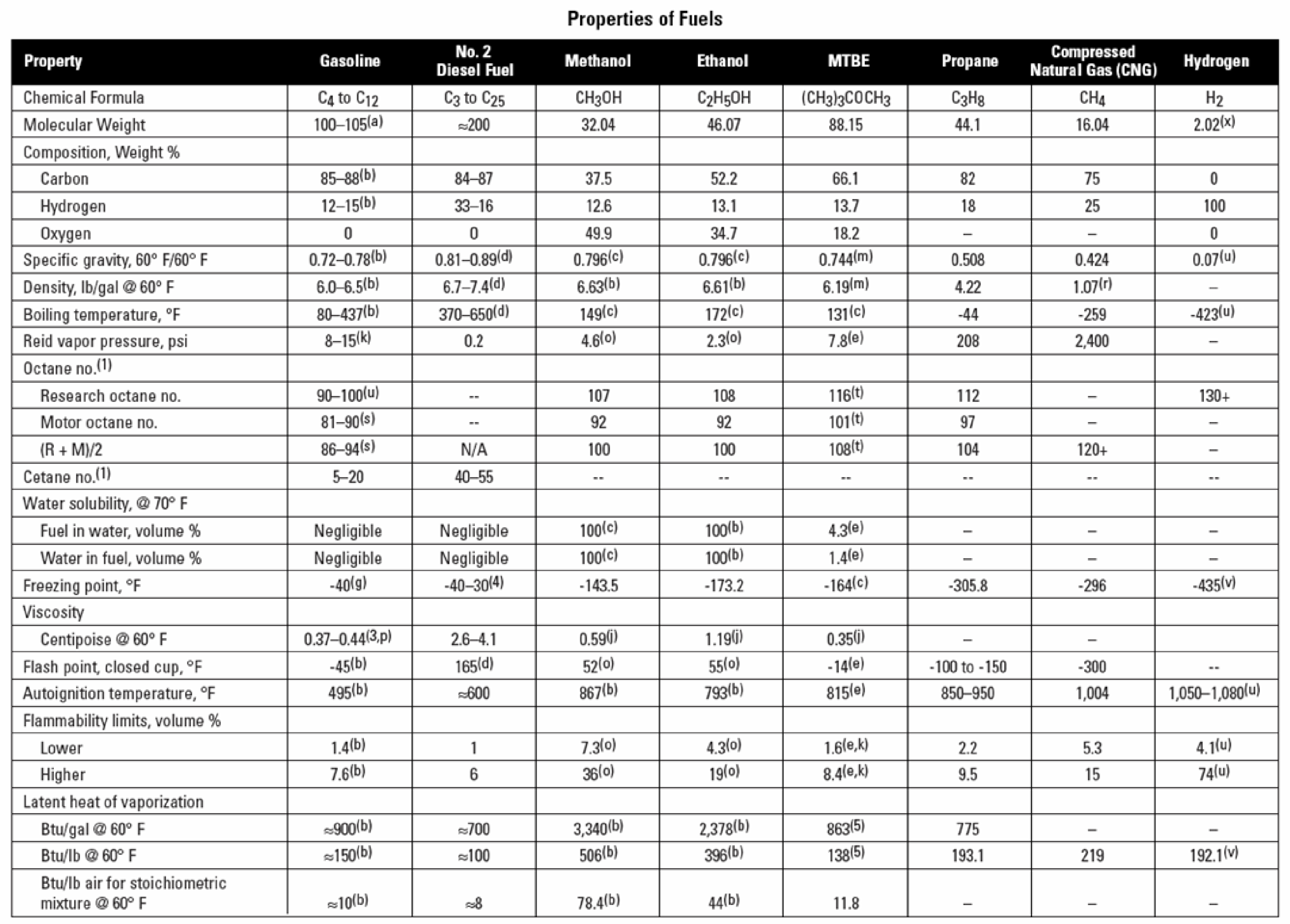
d: National Renewable Energy Laboratory goal

e: Multi-junction single crystal gallium arsenide solar cells and alkaline electrolyzer

f: Direct thermal hydrogen process potential

Source: H-Ion Solar Company, W.R. Pyle, M.H.hays &A.L. Spivak

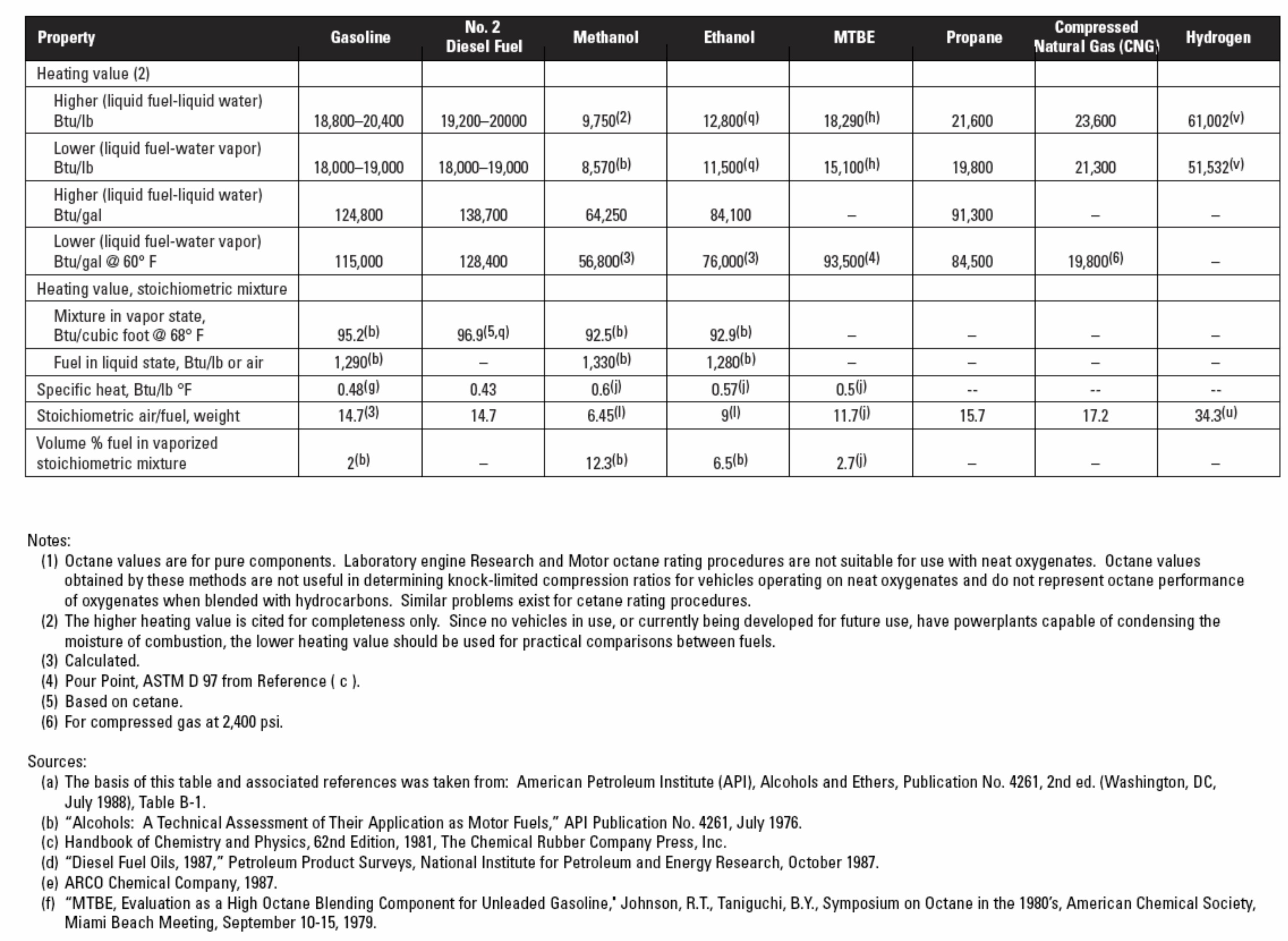
Fuel Properties



Properties of Fuels

Property	Gasoline	No. 2 Diesel Fuel	Methanol	Ethanol	MTBE	Propane	Compressed Natural Gas (CNG)	Hydrogen
Chemical Formula	C_4 to C_{12}	C_3 to C_{25}	CH_3OH	C_2H_5OH	$(CH_3)_3COCH_3$	C_3H_8	CH_4	H_2
Molecular Weight	100–105(a)	≈200	32.04	46.07	88.15	44.1	16.04	2.02(x)
Composition, Weight %								
Carbon	85–88(b)	84–87	37.5	52.2	66.1	82	75	0
Hydrogen	12–15(b)	33–16	12.6	13.1	13.7	18	25	100
Oxygen	0	0	49.9	34.7	18.2	–	–	0
Specific gravity, 60° F/60° F	0.72–0.78(b)	0.81–0.89(d)	0.796(c)	0.796(c)	0.744(m)	0.508	0.424	0.07(u)
Density, lb/gal @ 60° F	6.0–6.5(b)	6.7–7.4(d)	6.63(b)	6.61(b)	6.19(m)	4.22	1.07(r)	–
Boiling temperature, °F	80–437(b)	370–650(d)	149(c)	172(c)	131(c)	-44	-259	-423(u)
Reid vapor pressure, psi	8–15(k)	0.2	4.6(o)	2.3(o)	7.8(e)	208	2,400	–
Octane no.(1)								
Research octane no.	90–100(u)	--	107	108	116(t)	112	–	130+
Motor octane no.	81–90(s)	--	92	92	101(t)	97	–	–
(R + M)/2	86–94(s)	N/A	100	100	108(t)	104	120+	–
Cetane no.(1)	5–20	40–55	--	--	--	--	--	--
Water solubility, @ 70° F								
Fuel in water, volume %	Negligible	Negligible	100(c)	100(b)	4.3(e)	–	–	–
Water in fuel, volume %	Negligible	Negligible	100(c)	100(b)	1.4(e)	–	–	–
Freezing point, °F	-40(g)	-40–30(4)	-143.5	-173.2	-164(c)	-305.8	-296	-435(v)
Viscosity								
Centipoise @ 60° F	0.37–0.44(3,p)	2.6–4.1	0.59(j)	1.19(j)	0.35(j)	–	–	
Flash point, closed cup, °F	-45(b)	165(d)	52(o)	55(o)	-14(e)	-100 to -150	-300	--
Autoignition temperature, °F	495(b)	≈600	867(b)	793(b)	815(e)	850–950	1,004	1,050–1,080(u)
Flammability limits, volume %								
Lower	1.4(b)	1	7.3(o)	4.3(o)	1.6(e,k)	2.2	5.3	4.1(u)
Higher	7.6(b)	6	36(o)	19(o)	8.4(e,k)	9.5	15	74(u)
Latent heat of vaporization								
Btu/gal @ 60° F	≈900(b)	≈700	3,340(b)	2,378(b)	863(5)	775	–	–
Btu/lb @ 60° F	≈150(b)	≈100	506(b)	396(b)	138(5)	193.1	219	192.1(v)
Btu/lb air for stoichiometric mixture @ 60° F	≈10(b)	≈8	78.4(b)	44(b)	11.8	–	–	–

Fuel Properties



Property	Gasoline	No. 2 Diesel Fuel	Methanol	Ethanol	MTBE	Propane	Compressed Natural Gas (CNG)	Hydrogen
Heating value (2)								
Higher (liquid fuel-liquid water) Btu/lb	18,800–20,400	19,200–20000	9,750[2]	12,800[q]	18,290[h]	21,600	23,600	61,002[v]
Lower (liquid fuel-water vapor) Btu/lb	18,000–19,000	18,000–19,000	8,570[b]	11,500[q]	15,100[h]	19,800	21,300	51,532[v]
Higher (liquid fuel-liquid water) Btu/gal	124,800	138,700	64,250	84,100	–	91,300	–	–
Lower (liquid fuel-water vapor) Btu/gal @ 60° F	115,000	128,400	56,800[3]	76,000[3]	93,500[4]	84,500	19,800[6]	–
Heating value, stoichiometric mixture								
Mixture in vapor state, Btu/cubic foot @ 68° F	95.2[b]	96.9[5,q]	92.5[b]	92.9[b]	–	–	–	–
Fuel in liquid state, Btu/lb or air	1,290[b]	–	1,330[b]	1,280[b]	–	–	–	–
Specific heat, Btu/lb °F	0.48[g]	0.43	0.6[j]	0.57[j]	0.5[j]	--	--	--
Stoichiometric air/fuel, weight	14.7[3]	14.7	6.45[l]	9[l]	11.7[j]	15.7	17.2	34.3[u]
Volume % fuel in vaporized stoichiometric mixture	2[b]	–	12.3[b]	6.5[b]	2.7[j]	–	–	–

Notes:

(1) Octane values are for pure components. Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with hydrocarbons. Similar problems exist for cetane rating procedures.

(2) The higher heating value is cited for completeness only. Since no vehicles in use, or currently being developed for future use, have powerplants capable of condensing the moisture of combustion, the lower heating value should be used for practical comparisons between fuels.

(3) Calculated.

(4) Pour Point, ASTM D 97 from Reference (c).

(5) Based on cetane.

(6) For compressed gas at 2,400 psi.

Sources:

(a) The basis of this table and associated references was taken from: American Petroleum Institute (API), Alcohols and Ethers, Publication No. 4261, 2nd ed. (Washington, DC, July 1988), Table B-1.

(b) “Alcohols: A Technical Assessment of Their Application as Motor Fuels,” API Publication No. 4261, July 1976.

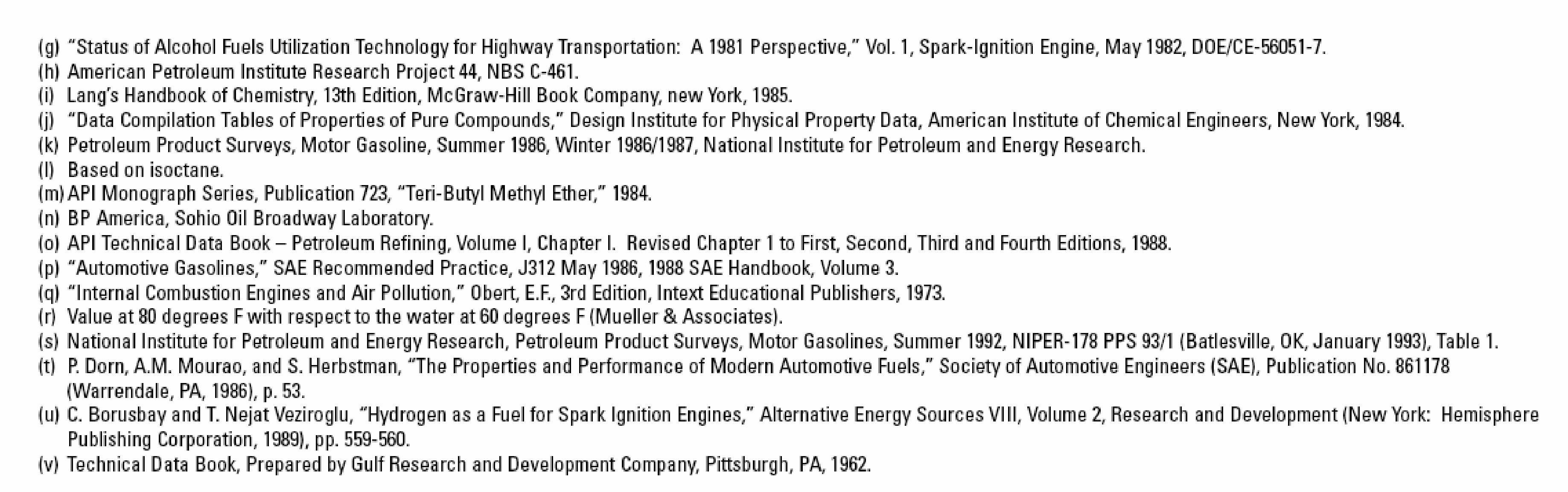
(c) Handbook of Chemistry and Physics, 62nd Edition, 1981, The Chemical Rubber Company Press, Inc.

(d) “Diesel Fuel Oils, 1987,” Petroleum Product Surveys, National Institute for Petroleum and Energy Research, October 1987.

(e) ARCO Chemical Company, 1987.

(f) “MTBE, Evaluation as a High Octane Blending Component for Unleaded Gasoline,' Johnson, R.T., Taniguchi, B.Y., Symposium on Octane in the 1980’s, American Chemical Society, Miami Beach Meeting, September 10-15, 1979.

Fuel Properties



(g) "Status of Alcohol Fuels Utilization Technology for Highway Transportation: A 1981 Perspective," Vol. 1, Spark-Ignition Engine, May 1982, DOE/CE-56051-7.
(h) American Petroleum Institute Research Project 44, NBS C-461.
(i) Lang's Handbook of Chemistry, 13th Edition, McGraw-Hill Book Company, new York, 1985.
(j) "Data Compilation Tables of Properties of Pure Compounds," Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York, 1984.
(k) Petroleum Product Surveys, Motor Gasoline, Summer 1986, Winter 1986/1987, National Institute for Petroleum and Energy Research.
(l) Based on isoctane.
(m) API Monograph Series, Publication 723, "Teri-Butyl Methyl Ether," 1984.
(n) BP America, Sohio Oil Broadway Laboratory.
(o) API Technical Data Book – Petroleum Refining, Volume I, Chapter I. Revised Chapter 1 to First, Second, Third and Fourth Editions, 1988.
(p) "Automotive Gasolines," SAE Recommended Practice, J312 May 1986, 1988 SAE Handbook, Volume 3.
(q) "Internal Combustion Engines and Air Pollution," Obert, E.F., 3rd Edition, Intext Educational Publishers, 1973.
(r) Value at 80 degrees F with respect to the water at 60 degrees F (Mueller & Associates).
(s) National Institute for Petroleum and Energy Research, Petroleum Product Surveys, Motor Gasolines, Summer 1992, NIPER-178 PPS 93/1 (Batlesville, OK, January 1993), Table 1.
(t) P. Dorn, A.M. Mourao, and S. Herbstman, "The Properties and Performance of Modern Automotive Fuels," Society of Automotive Engineers (SAE), Publication No. 861178 (Warrendale, PA, 1986), p. 53.
(u) C. Borusbay and T. Nejat Veziroglu, "Hydrogen as a Fuel for Spark Ignition Engines," Alternative Energy Sources VIII, Volume 2, Research and Development (New York: Hemisphere Publishing Corporation, 1989), pp. 559-560.
(v) Technical Data Book, Prepared by Gulf Research and Development Company, Pittsburgh, PA, 1962.