



60 Years of Liquid Hydrogen: Revolutionizing our Clean Energy Future Across the Solar System

NASA Cryogenics Webcast -- June 22nd, 2022

In this talk:

1. Past, present, future of H₂
2. Liquefaction basics
3. LH₂ storage.
4. NASA's opportunity

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H
H **Y** **d**rogen
P roperties for
E nergy
R esearch *Lab*

¹
H
1.00794

Hydrogen: first element of the Universe.

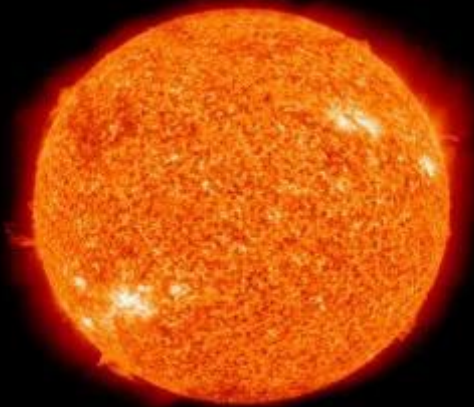


Kardashev Level 3

Humanity's evolution has always been and will always continue to be about mastering hydrogen.

13.7B Years Ago
74% of mass in the Universe.

Kardashev Level 2



4.6B Years Ago
75% of mass in the Sun.

Kardashev Level 1



4.35B Years Ago
13% of atoms on Earth

Kardashev Level 0



3.35B Years Ago
Key driver of chemical processes.



¹H
1.00794

Hydrogen: first for flight.



1783: First H₂ balloon flights

Hydrogen has always been, and will continue to be, the first for flight.



1957: Project Sulton tests Model 304 LH₂ engine

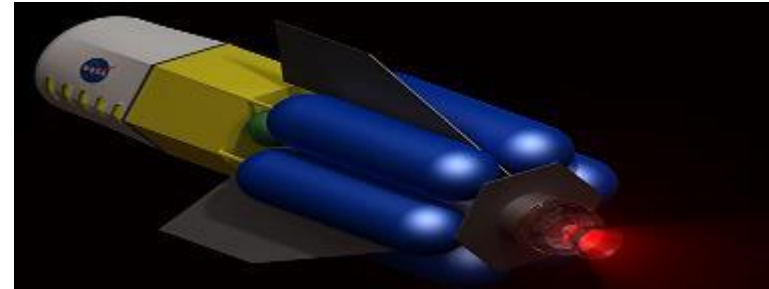


1958: RL-10 & J-2 predecessor development begins

2050:
Fusion H₂

2035:
Nuclear H₂

1981:
Shuttle (Chemical)



¹H
1.00794

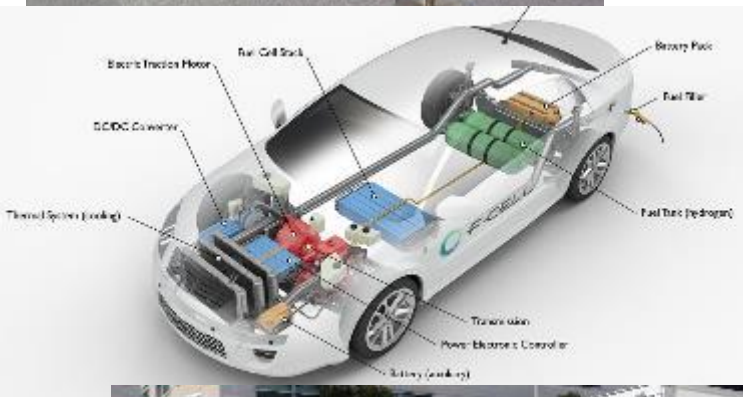
Hydrogen: the future of freight.



30% of all retail food and groceries in the US are moved by hydrogen fueled vehicles.



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1.1 DOE's

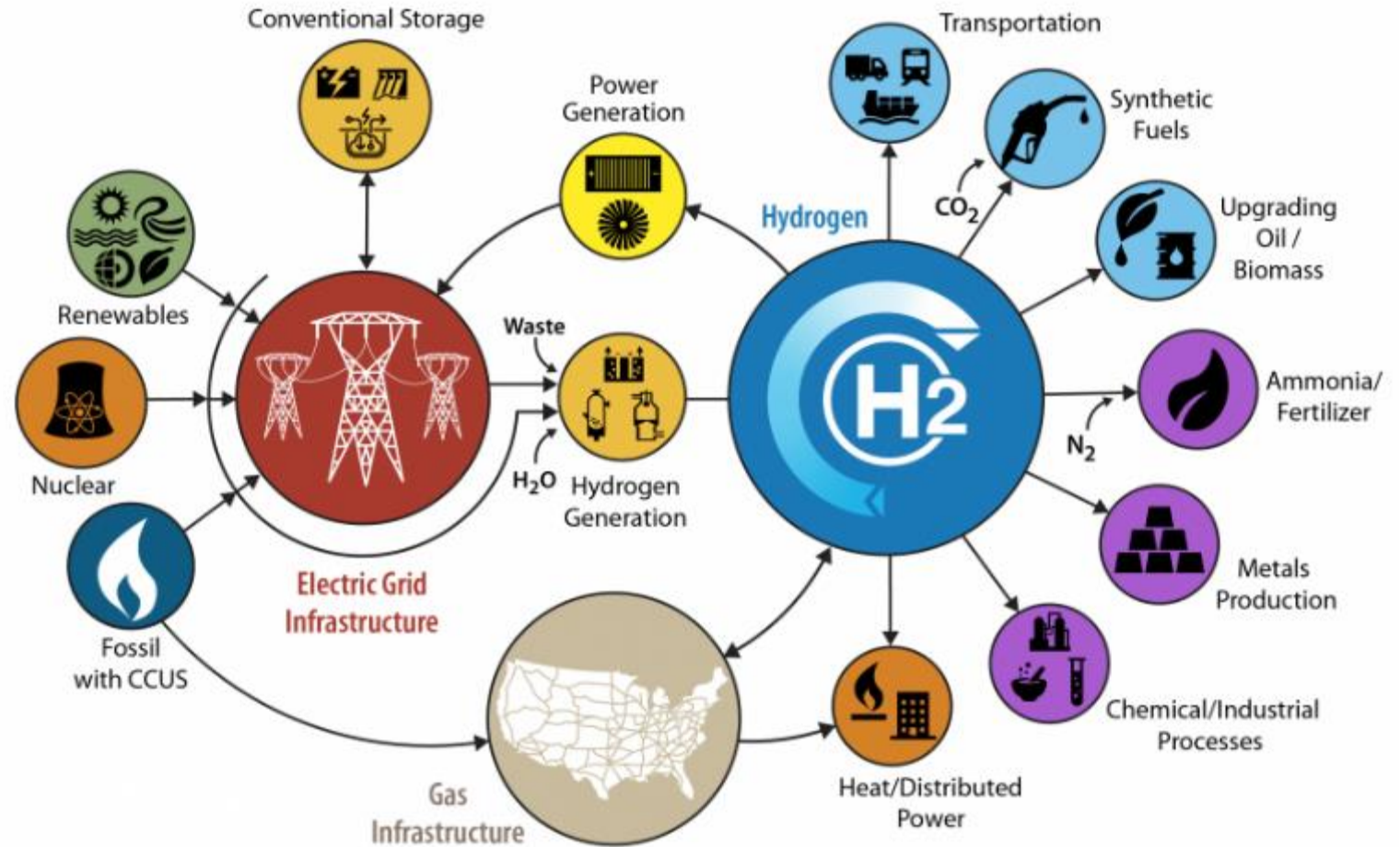


Hydrogen

From the DOE's HydrogenShot website:

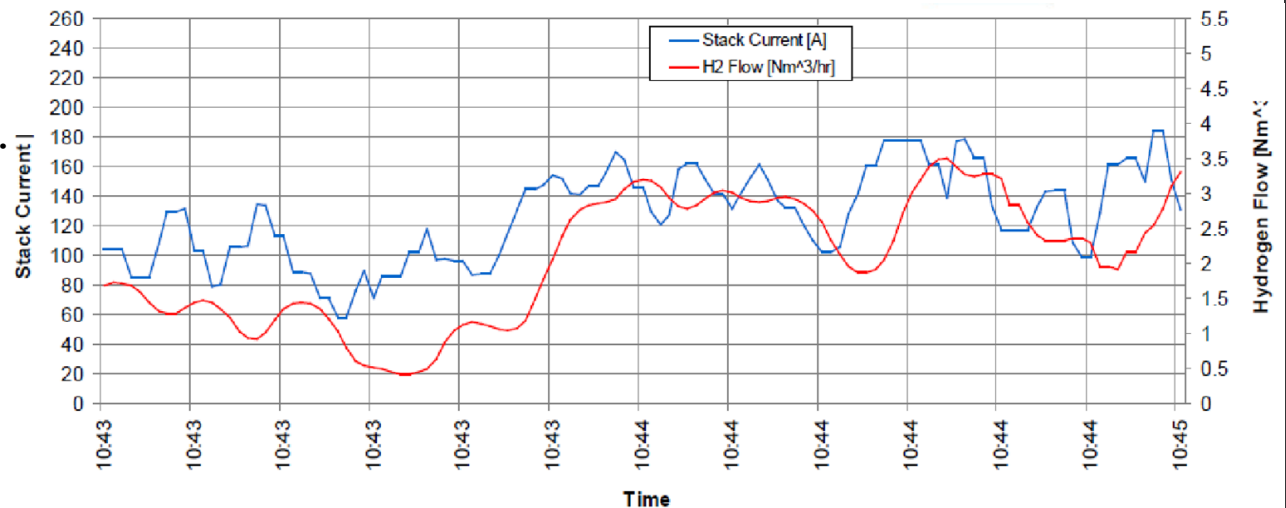
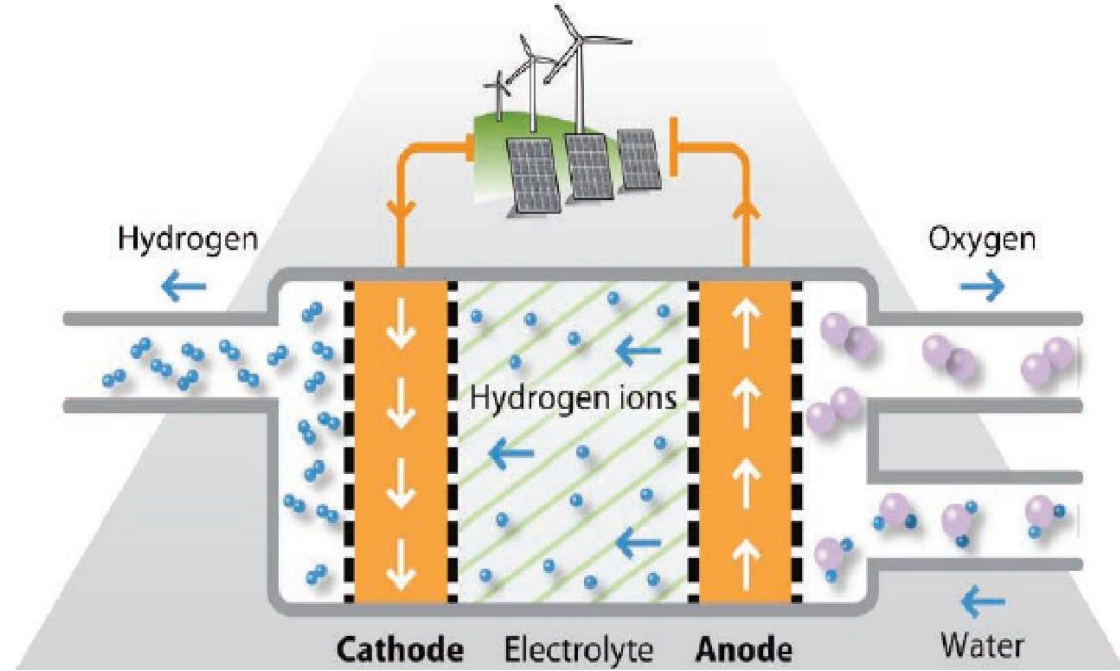
“The first Energy Earthshot, launched June 7, 2021—Hydrogen Shot—seeks to reduce the cost of clean hydrogen by 80% to \$1 per 1 kilogram in 1 decade ("1 1 1").”

H2 Infrastructure bill increases federal expenditures ~40x.



1.2 Making H₂ green – electrolyzers

- NREL's wind-to-hydrogen project has demonstrated for over a decade that wind turbines can produce hydrogen via electrolysis.
- DOE recent review of current 1500 kgH₂/day distributed PEM electrolyzer plant costs:
 - Total CapEx: \$1450/kW
 - Production Efficiency: 50.4 kW-hr/kgH₂
 - H₂ production cost: \$4.98/kgH₂
- Key hidden advance is electrochemical compression → >90% efficiency up to 10 MPa.



<https://www.nrel.gov/hydrogen/wind-to-hydrogen.html>

https://www.hydrogen.energy.gov/pdfs/19009_h2_production_cost_pem_electrolysis_2019.pdf

1.3 Electrolyzer trends vs. solar & wind

- Fuel Cell production capacities are scaling similarly to solar and wind, just coming decades later.
- Solar and wind are now the cheapest sources of energy. However, the intermittency of these energy forms necessitates storage, which is driving lithium battery and hydrogen production capacities.

Early Wind, Solar, Fuel Cell and Electrolyzer Production (MW)

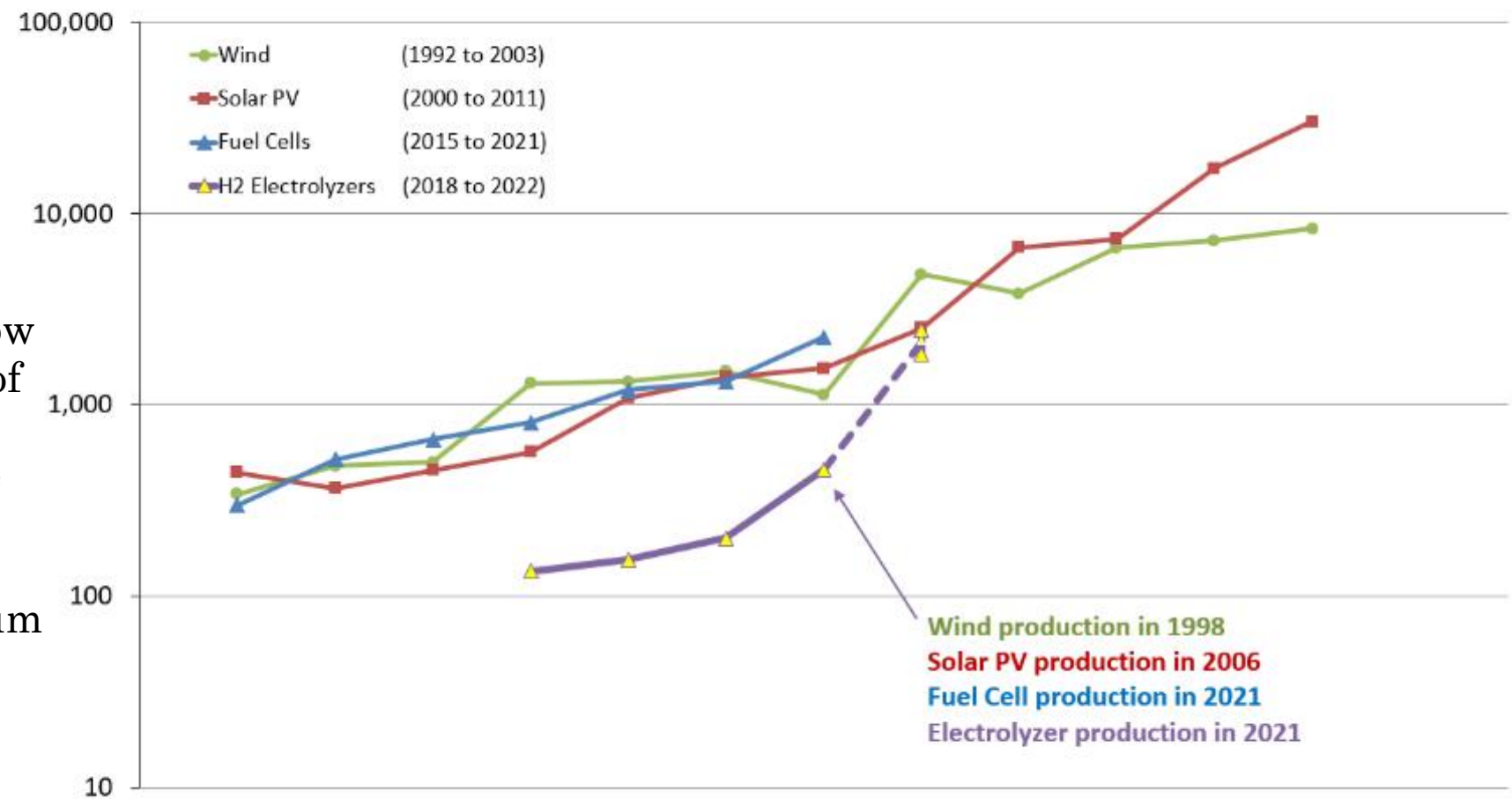
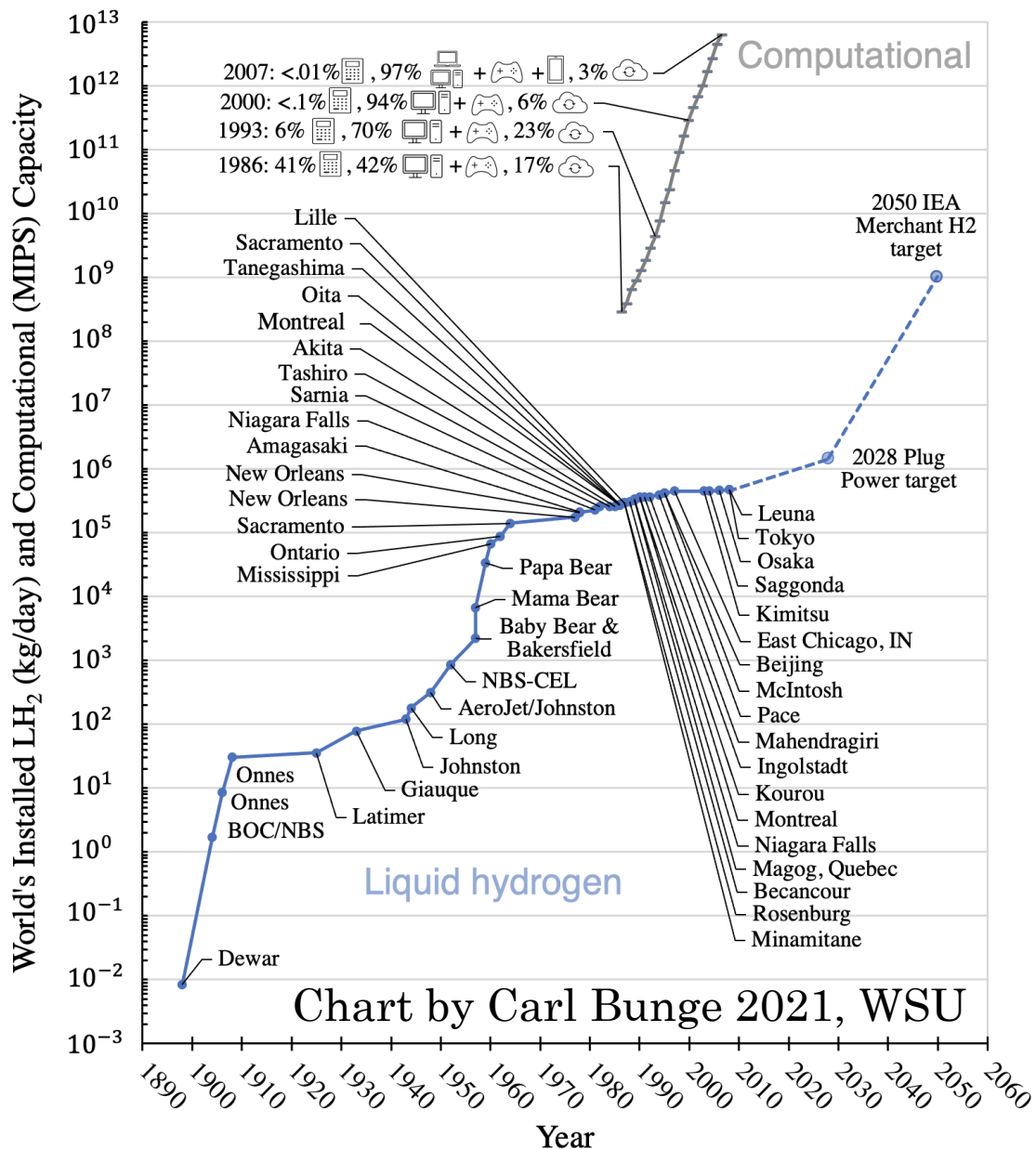


chart: M Klippenstein (@ElectronComm). Data: Wikipedia, E4Tech, Bernstein Research, BNEF (electrolyzers).

1.4 Liquid hydrogen trends



- Just 8 hydrogen liquefiers served the needs of NASA and US industry for ~50 years.
- 80-90% of non-pipeline H₂ delivered by liquid tanker truck.¹
- Since 2015 more than 8 new hydrogen liquefiers have been announced effectively increasing US capacity more than 50%. More are being upgraded to produce green hydrogen.
- Each phase of rapid growth was enabled by a technological breakthrough.
- We must rapidly advance hydrogen liquefaction technology research in order to avert the most catastrophic effects of climate change.

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Our coming LH₂ logistical challenge

- If I put \$100M on the table, I'd receive proposals to build hydrogen liquefiers operating between 30-40% of what is theoretically possible.
- If I stored my liquid hydrogen for later use, the hydrogen utilization would range between 60-93%, the rest would be lost due to boil-off.
- These values have remained mostly unchanged over the last 60 years.

Sustainable living on Earth and across our Solar System likely depends on solving this liquid hydrogen logistics challenge.





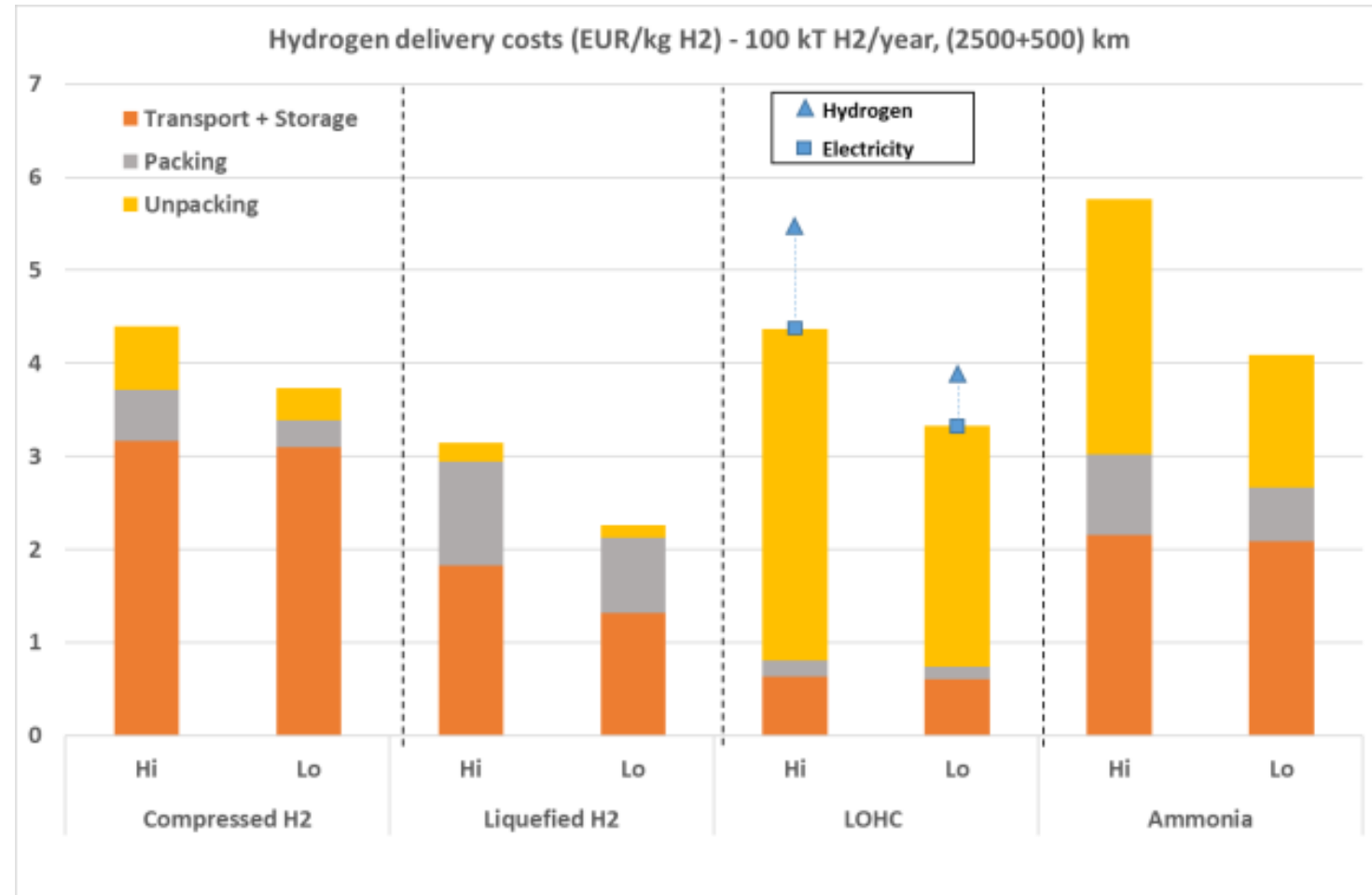
2. Liquefaction Basics

1. Why liquid hydrogen?
2. Fundamentals of hydrogen
3. Fundamentals of refrigeration
4. Opportunities for change
5. 3 new concepts for liquefaction



2.1 Hydrogen logistical paradigms

- June 6th study from EU compared distribution costs for multiple pathways. Assuming 100,000 tonnes/year delivered to refueling station network in 1500 mile radius.
- Hydrogen pipeline costs were comparable to compressed or liquefied hydrogen in the 1,000,000 tonnes/year case.
- 1 euro = \$1.18 USD





2.1 LH₂ goes the distance

- Over a wide range of practical delivery scenarios, even to a single end-point user, liquid hydrogen is the most cost effective option.
- Zero-Boil-Off (ZBO) could substantially improve the logistics of hydrogen and large-scale seasonal energy storage.

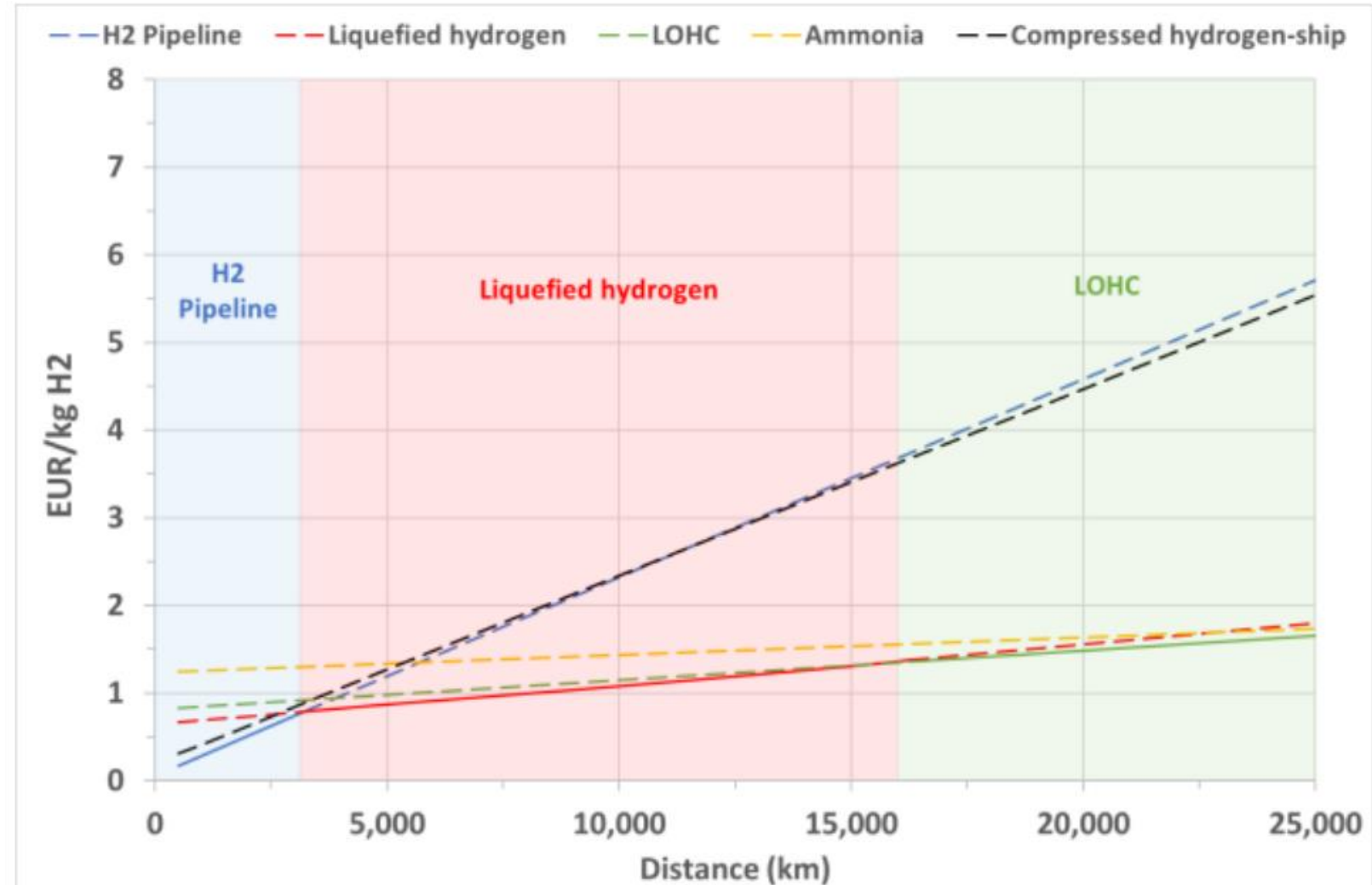
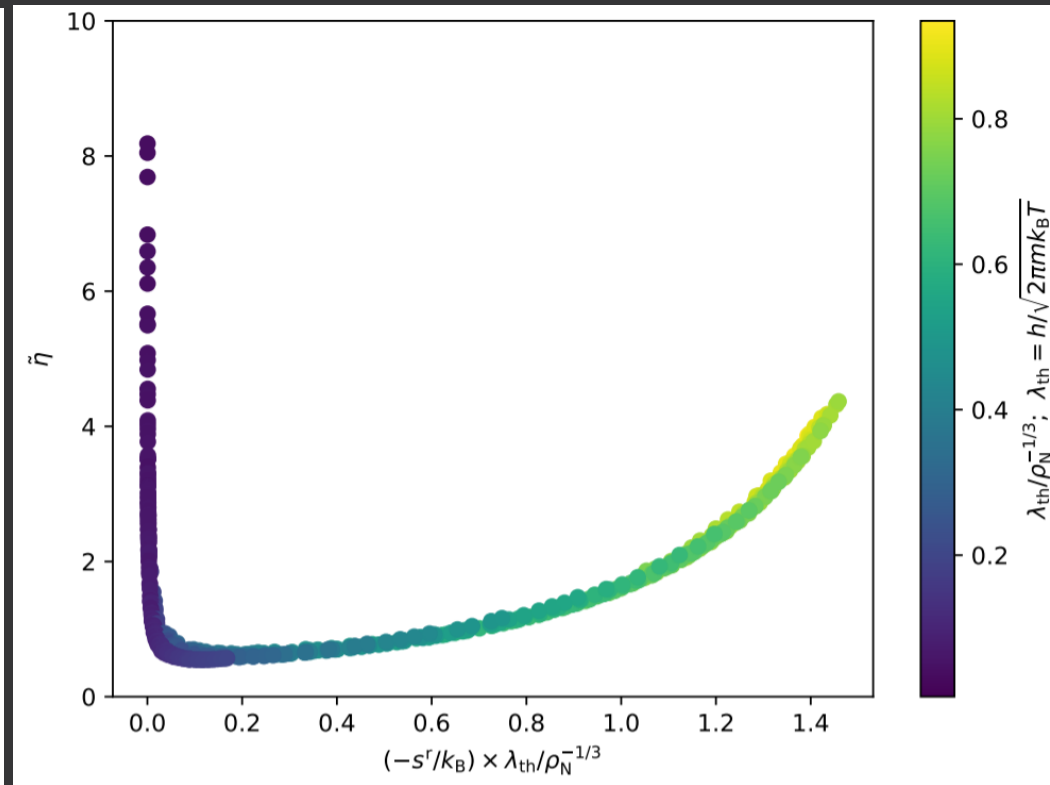
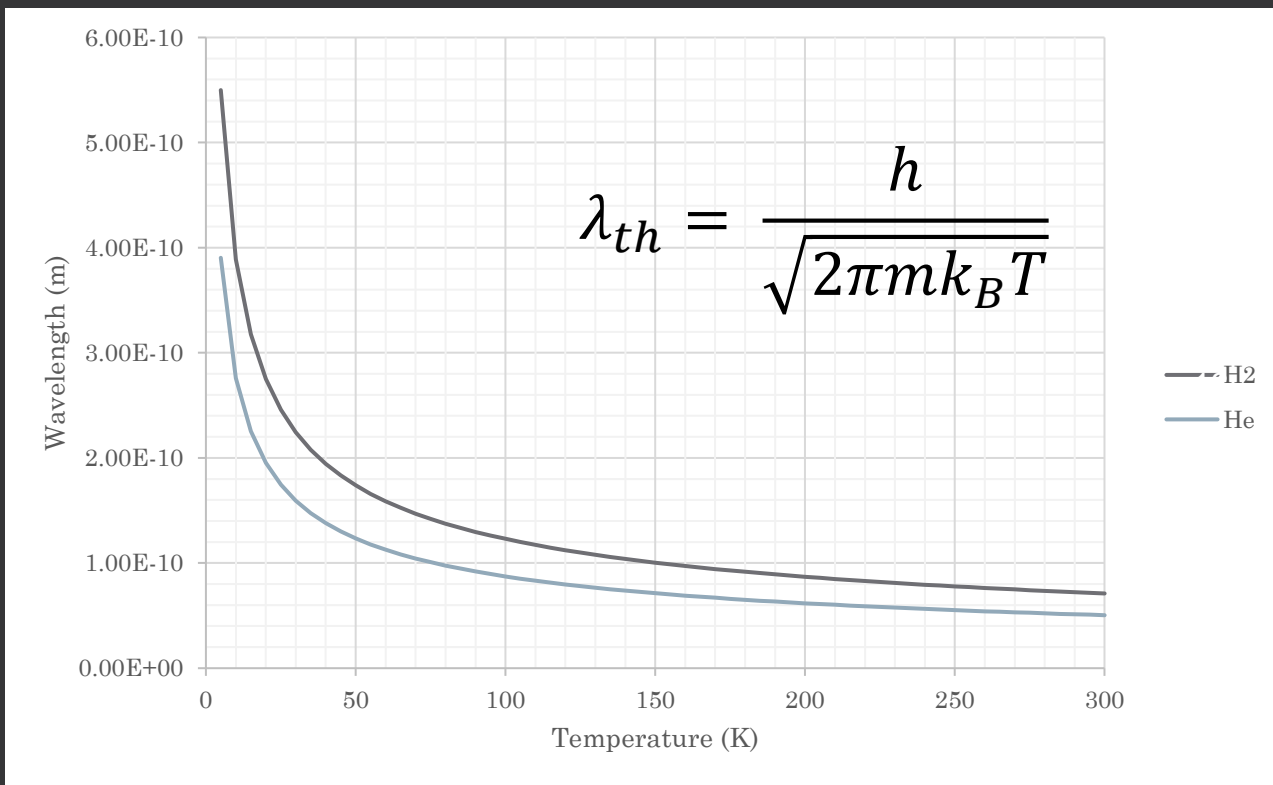


Figure 2 Hydrogen delivery costs for a simple (point to point) transport route, for 1 Mt H₂ and low electricity cost scenario.

2.3 Novel H₂ physics: quantum swelling

- In 1929, Louis de Broglie won the Nobel Prize: “for his discovery of the wave nature of electrons.” (Nobelprize.org)
- He, H₂, Ne have a small enough momentum to allow wavelengths much larger than the average distance between molecular interactions.



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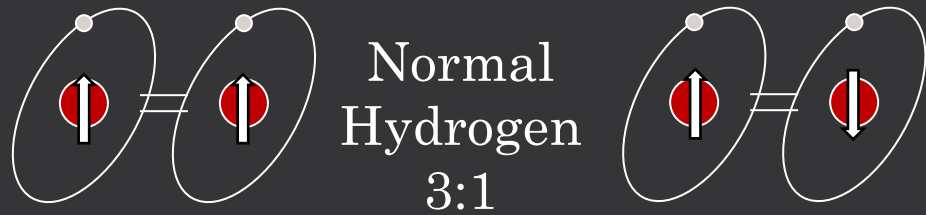
2.3 Novel H₂ physics: nuclear-spin isomers

In 1932, Werner Heisenberg won the Nobel Prize:

“for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen.”



¹Nobelprize.org accessed 2010

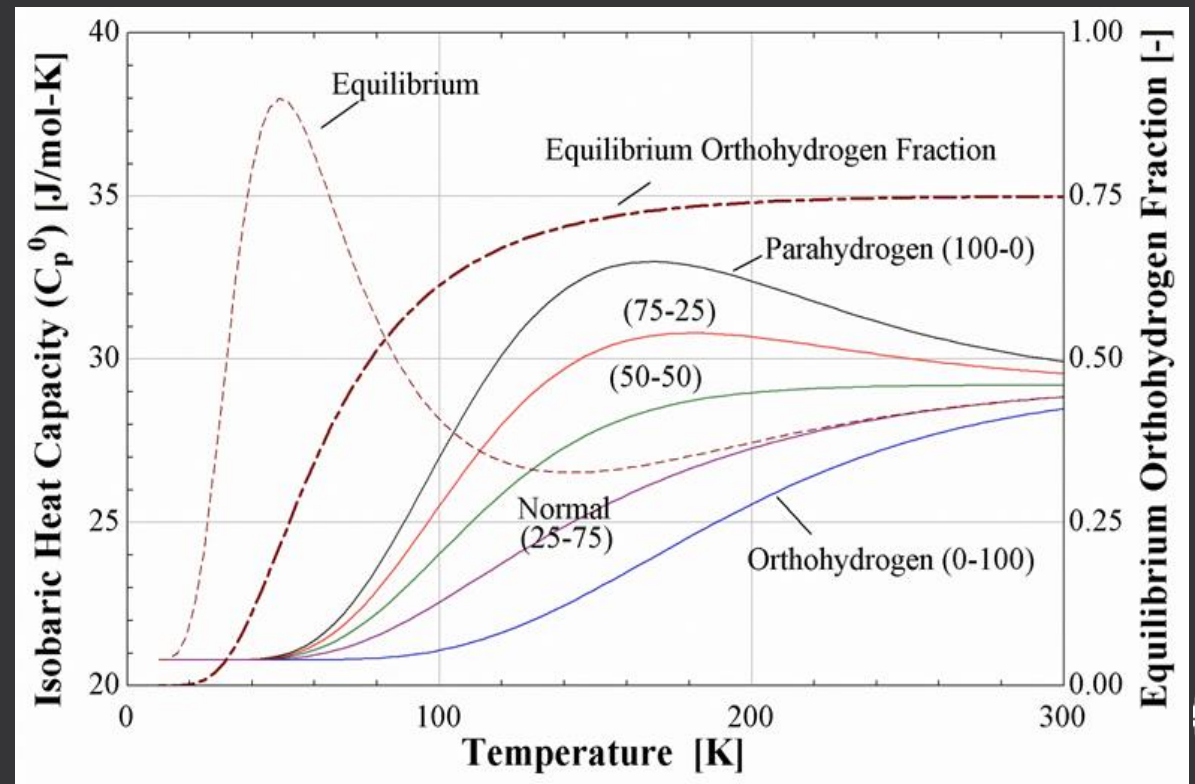


$$\psi_{tot} (antisym) = (\psi_{vib} sym) (\psi_{rot} antisym) (\psi_{spin} sym)$$

$$\psi_{rot} = 1, 3, 5, \dots$$

$$\psi_{tot} (antisym) = (\psi_{vib} sym) (\psi_{rot} sym) (\psi_{spin} antisym)$$

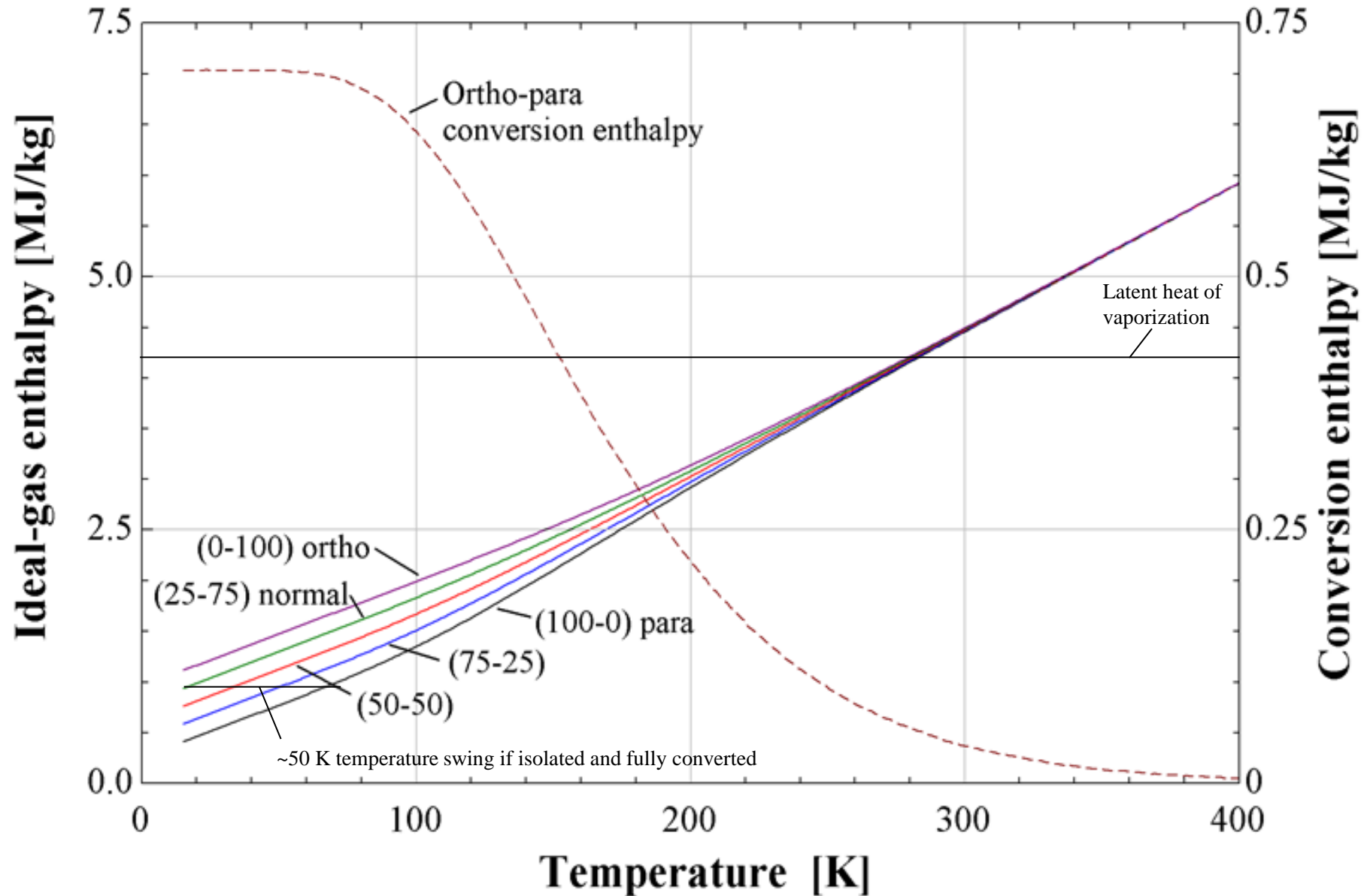
$$\psi_{rot} = 0, 2, 4, \dots$$



HYPER



2.3 Ortho-para effects on properties: enthalpy



2.3 Fundamentals of refrigeration

- 1st Law Efficiency

$$COP_I = \frac{\text{What you paid}}{\text{What you want}}$$

- Carnot (ideal) Efficiency

$$COP_C = \frac{T_C}{(T_H - T_C)}$$

- 2nd Law (exergetic) Efficiency

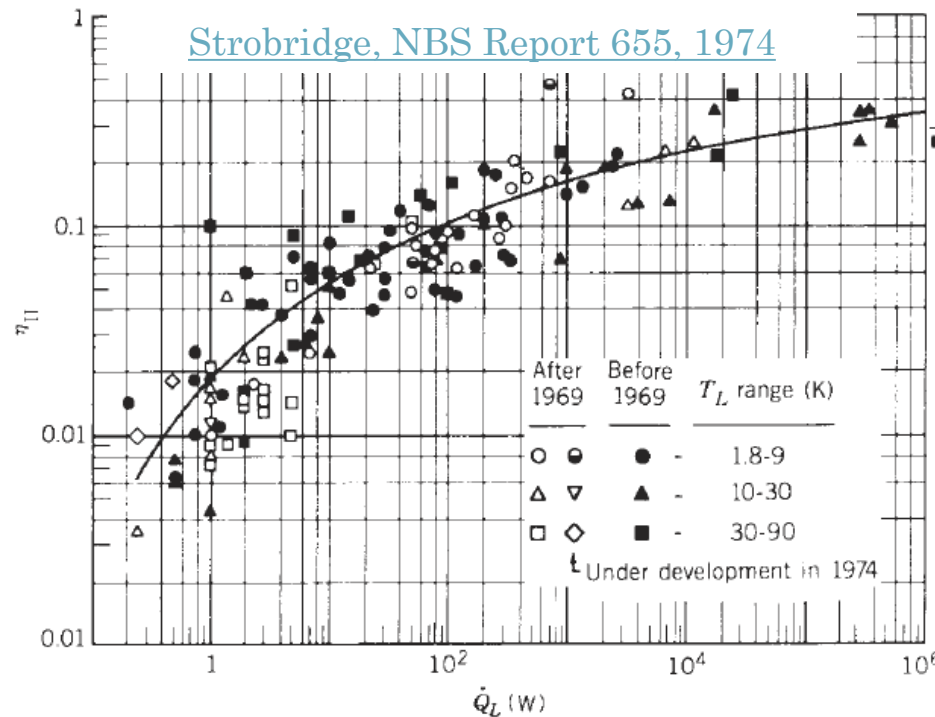
$$COP_{II} = \frac{\text{Best you could've}}{\text{How you did}} = \frac{COP_C}{COP_I}$$

- Spending electric exergy to obtain 1 kg of LH2 so units become kW-hr/kg.

- LH2: $COP_C = 21/(300-21) = 0.075$ or 3.92 kW-hr/kg

- LH2 $COP_{II} = 3.92/13 = 29.7\%$

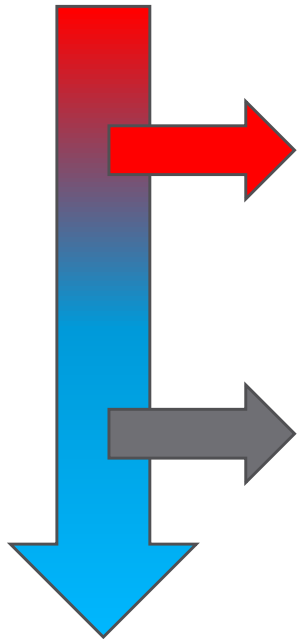
- Also known as specific energy consumption (SEC)
- Legacy H2 liquefiers have SEC ~ 13 kW-hr/kg.
- Current H2 liquefiers targeting 9-10 kW-hr/kg.



2.3 Fundamentals of refrigeration



1. Warm H₂ in
T=298 K
P= 1 atm
75% ortho



2. Remove entropy
via heat transfer

3. Remove enthalpy
via work transfer
(usually mechanical
or electrical work)

4. Cold H₂ out
T=20 K
P= 1.5 atm
0% ortho

• Only four ways to change the thermodynamic cycle for hydrogen liquefaction:

1. Change the input exergy
2. Change the heat transfer through entropy
3. Change the work transfer
4. Change the output exergy

$$\text{Flow Exergy: } \varphi = (h - h_0) - T_0(s - s_0)$$

$$\underbrace{4428}_{\text{kJ/kg}} \quad \underbrace{16921}_{\text{kJ/kg}}$$

Entropy contribution to exergy is 4x the enthalpy.

2.4 Opportunities: change the input



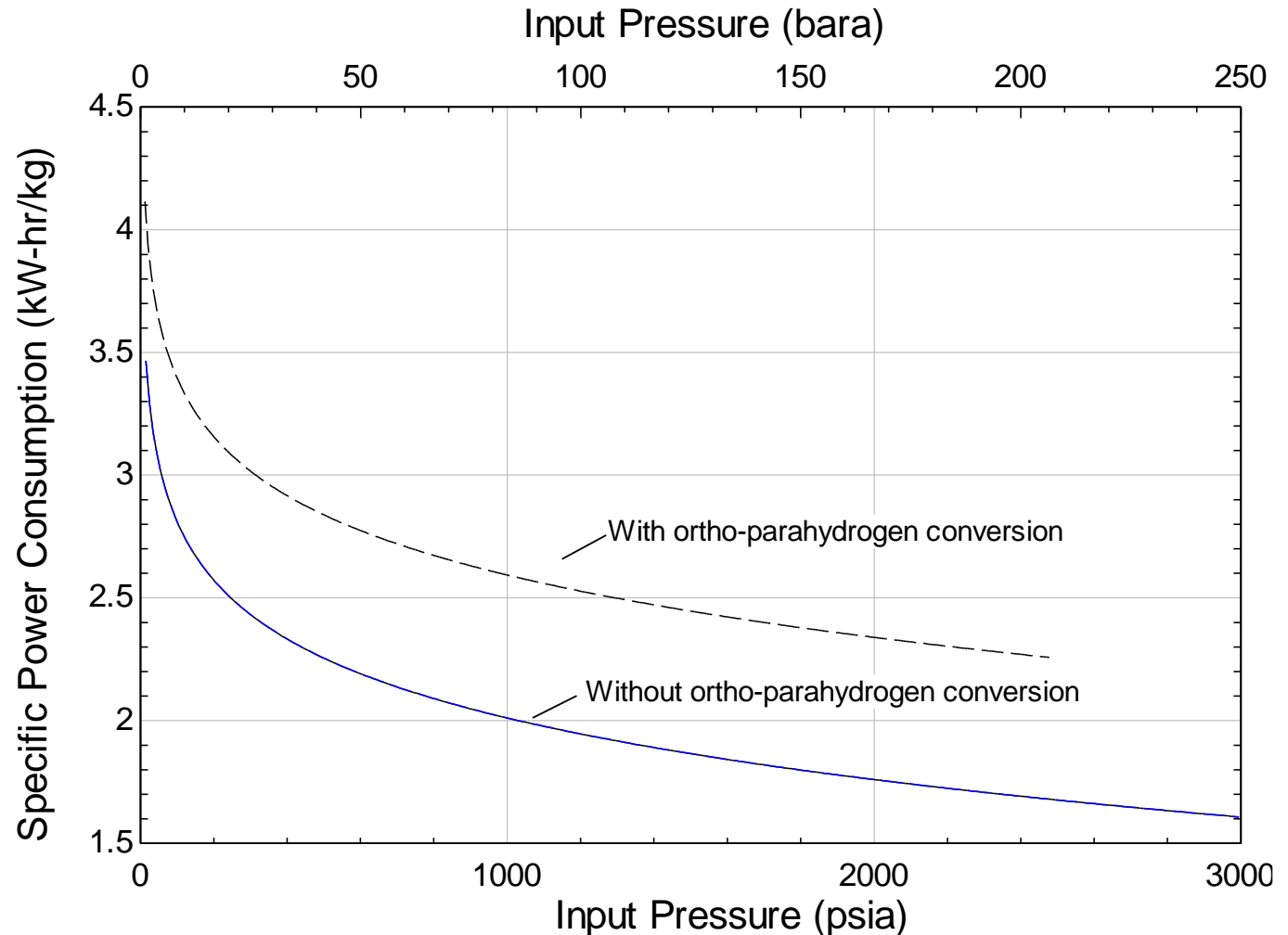
Warm H₂ in
T=298 K
P= 1 atm
75% ortho

- Increasing the exergy of the hydrogen flowing into the cycle via electrochemical compression, radiative cooling, or o-p separation can significantly reduce the SEC.

Remove entropy
via heat transfer

Remove enthalpy via
work transfer
(usually mechanical
or electrical work)

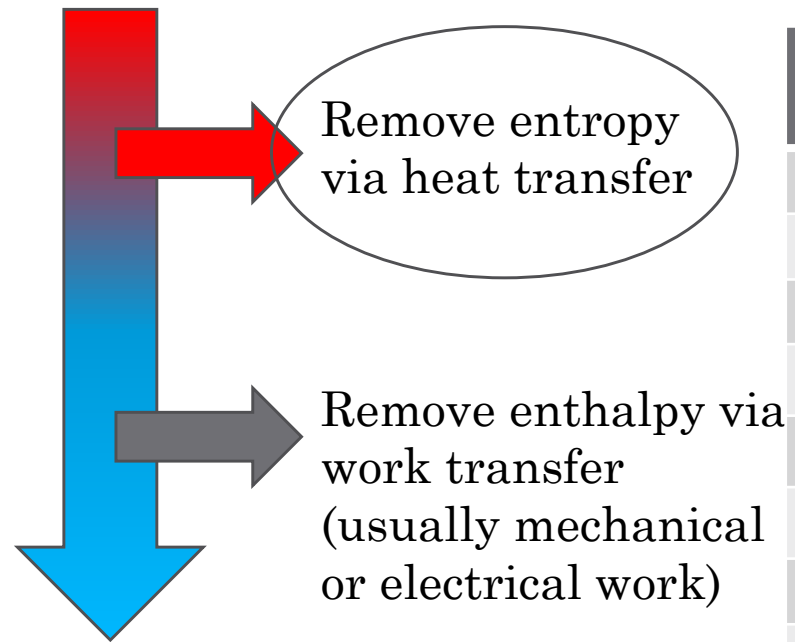
Cold H₂ out
T=20 K
P= 1.5 atm
0% ortho



2.4 Opportunities: change the entropy

Warm H₂ in
 T=298 K
 P= 1 atm
 75% ortho

- New materials are being created that allow for changes in entropy at constant temperature (phase change). Ability to control phase change, and phase change size are what controls the efficacy.



Cold H₂ out
 T=20 K
 P= 1.5 atm
 0% ortho

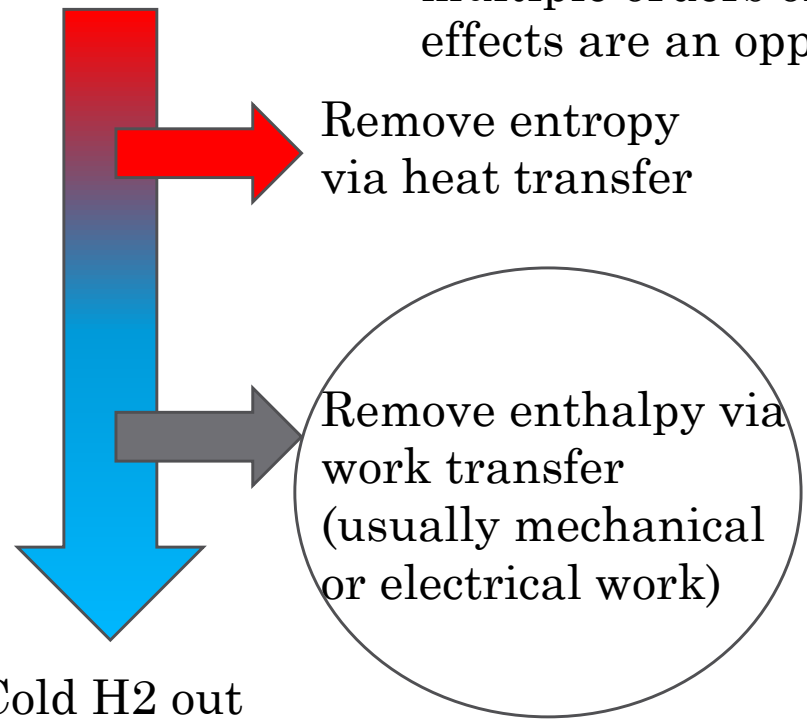
Endothermic Phase Change	Driving Force to Cause Change	Ordered Phase	Disordered Phase
Fluid	Pressure	Liquid	Gas
Fluid	Pressure	Solid	Liquid
Chemical	Chem. potential	Strong solution	Dilute solution
Chemical	Chem. potential	Precipitate	Uniform solution
Chemical	Surface tension	Bulk liquid	Surface film
Chemical/Physical	Sorption	(Ad/Ab)sorbed	Desorbed
Physical	Magnetic field	Anti-ferromagnet	Paramagnet
Physical	Magnetic field	Superconductor	Normal material
Physical	Electric field	Anti-ferroelectric	Paraelectric
Physical	Many	Ordered crystal	Disordered crystal
Physical	Unknown	Rotational order	Molecular rotation

2.4 Opportunities: change the enthalpy



Warm H2 in
 $T=298\text{ K}$
 $P=1\text{ atm}$
 75% ortho

- Cryogenic compressors and piston-expanders can improve the transfer of Pdv work. Requires novel seal and bearing designs for cryogenic hydrogen.
- Non-Pdv types are typically controlled by Arrhenius (thermal) diffusion which is multiple orders of magnitude slower at cryogenic temperatures. Quantum effects are an opportunity around this.



Cold H2 out
 $T=20\text{ K}$
 $P=1.5\text{ atm}$
 0% ortho

Work Transfer Type	Gradient Type	Device Type
Mechanical/Shaft	Pdv/Momentum	Turbomachinery
Mechanical/Shaft	Pdv	Piston/Impeller
Oscillatory pressure	Pdv	Linear driver
Oscillatory pressure	Pdv	Acoustic speaker
J-T expansion	Pdv	Throttle
Electrical	Voltage	Diode
Electrical	Temperature	Thermoelectric diode
Electrical	Chemical Potential	Fuel Cell/Electrolyzer
Induction	Magnetic field	Electric coil

HYPER

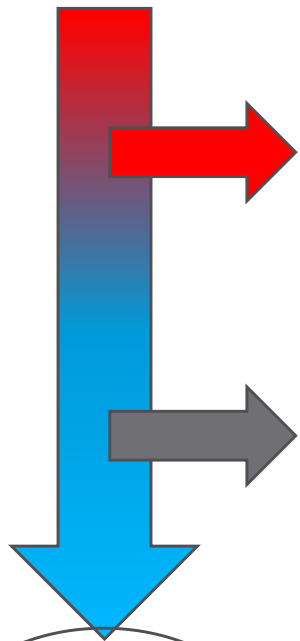


2.4 Opportunities: change the output

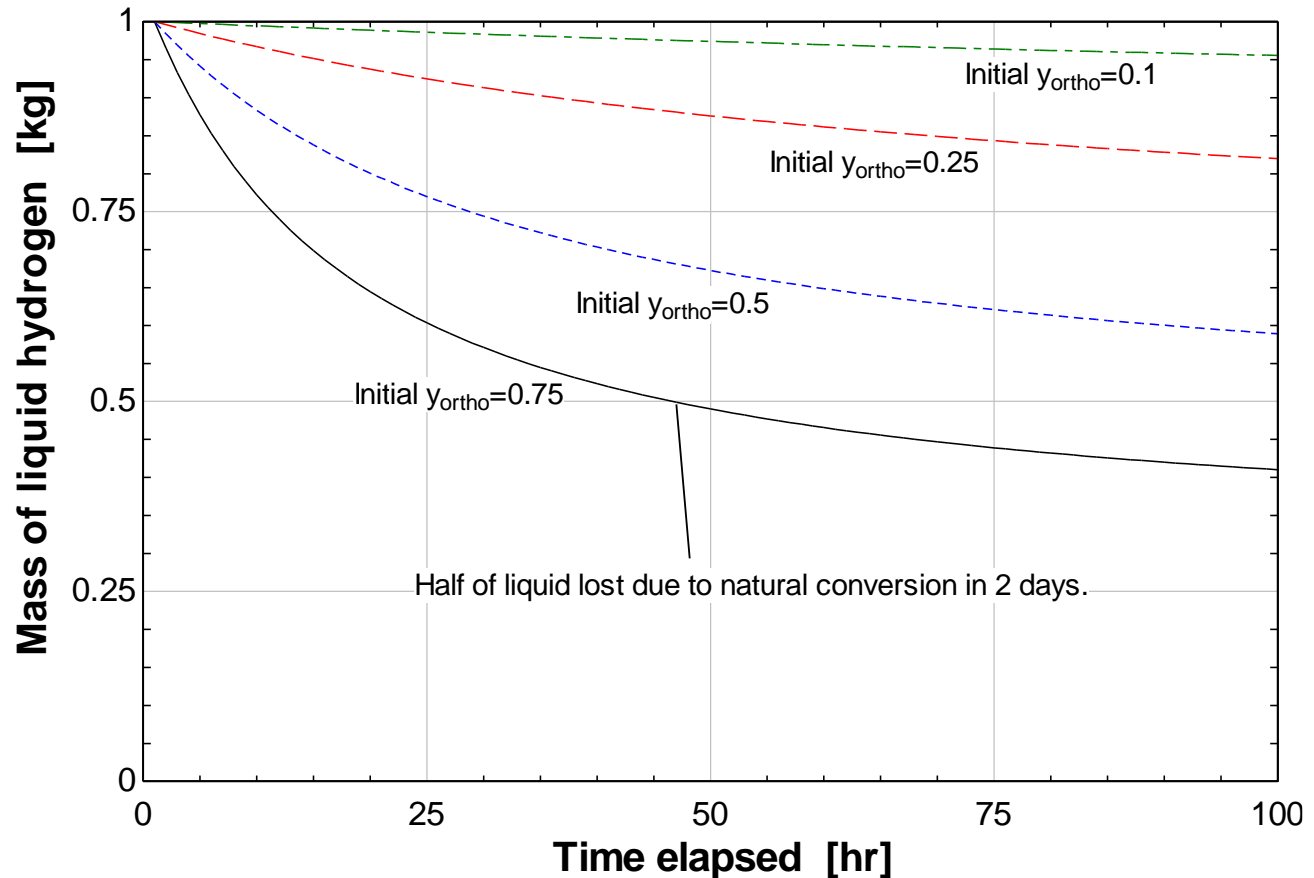


Warm H2 in
T=298 K
P= 1 atm
75% ortho

- Decrease the exergy of the hydrogen flowing out of the cycle via lower output exergy (higher temperature & pressure), and no o-p conversion (but with losses).
- The latent heat of vaporization, which controls liquid stability during transport, is 9% less at 25 K, 35% less at 30 K, 0 when supercritical. Ultimately more volatile.

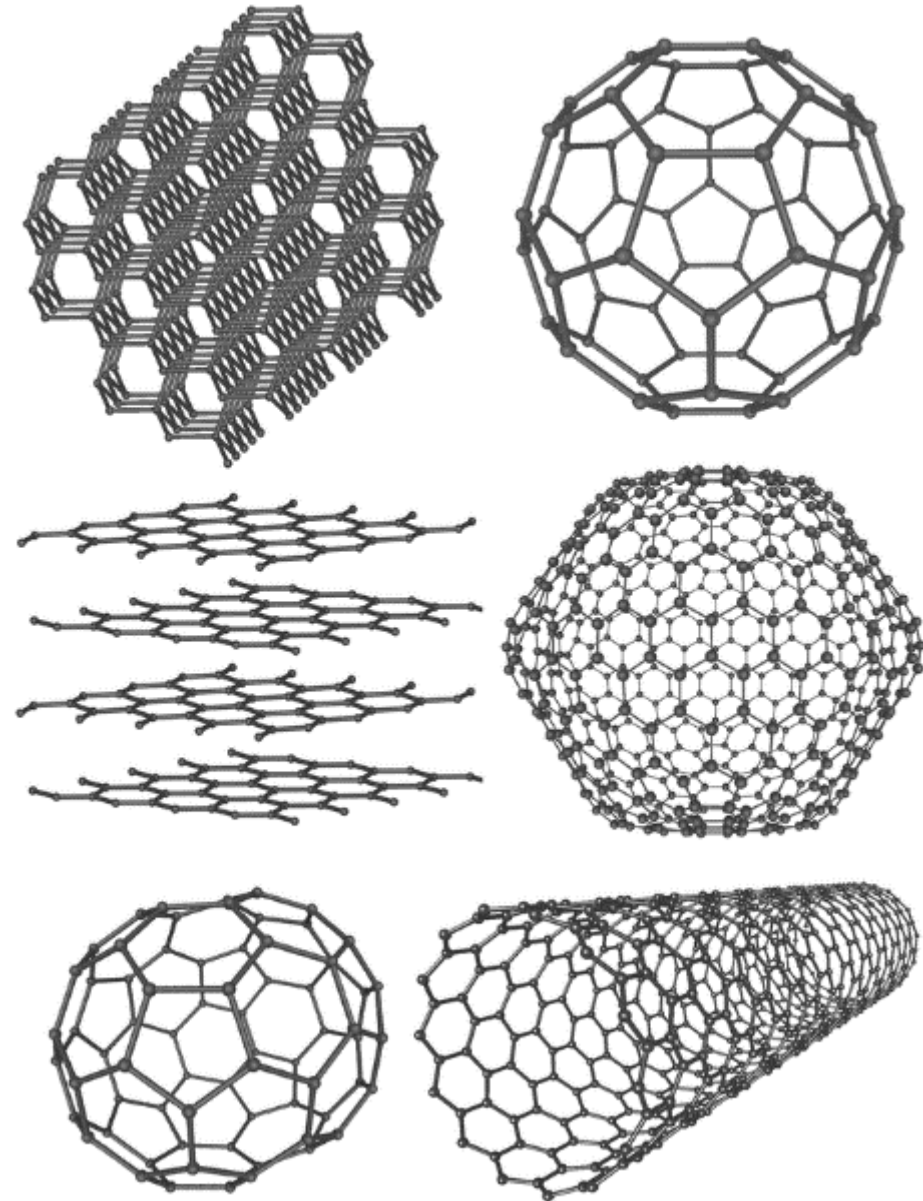


Cold H2 out
T=20 K
P= 1.5 atm
0% ortho



2.5 Quantum plumbing

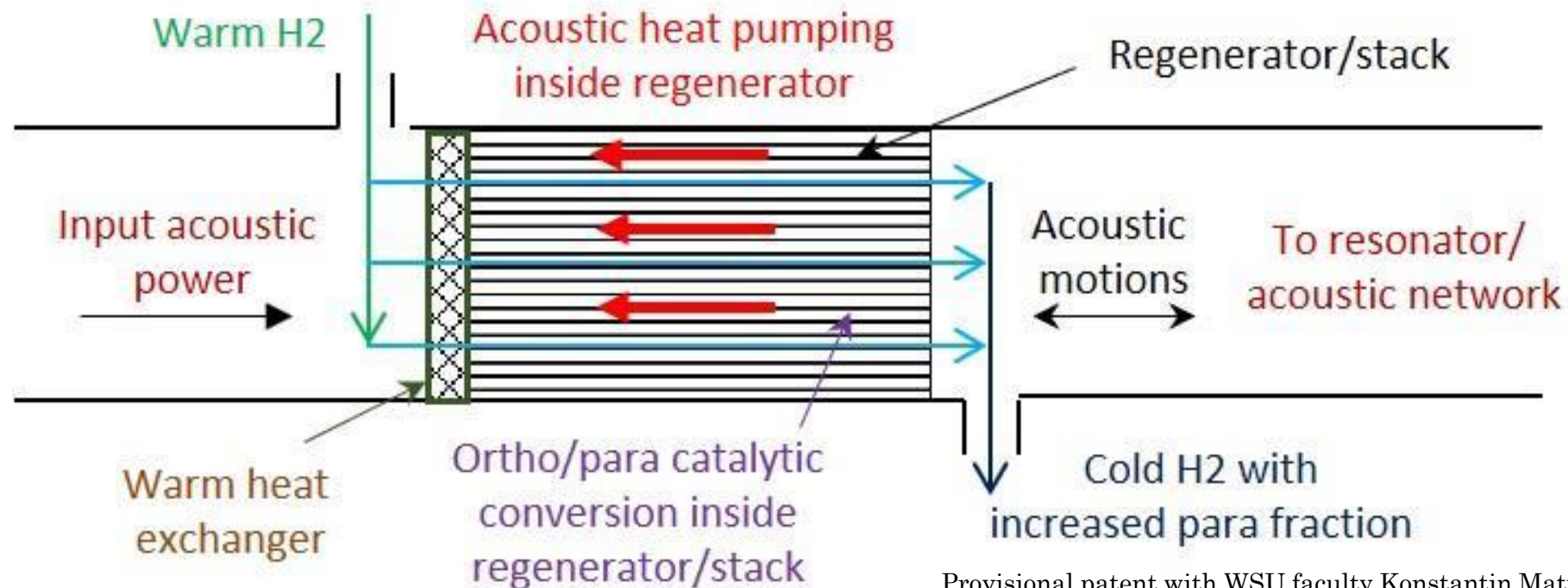
- The most challenging extreme of liquefaction occurs below 77 K when quantum effects begin to dominate over classical.
- Nanotube & film arrays are tunable over sensitive length-scales for cryogenic hydrogen.
- Orthohydrogen preferentially adsorbs on surfaces and can be separated creating opportunities for quantum sieving or tunneling assisted catalysis.
- Hydrogen quantum swelling could allow sieving of smaller molecules like neon for use in active dilution refrigeration cycles.
- Nanoscale check valves could improve pressure control.





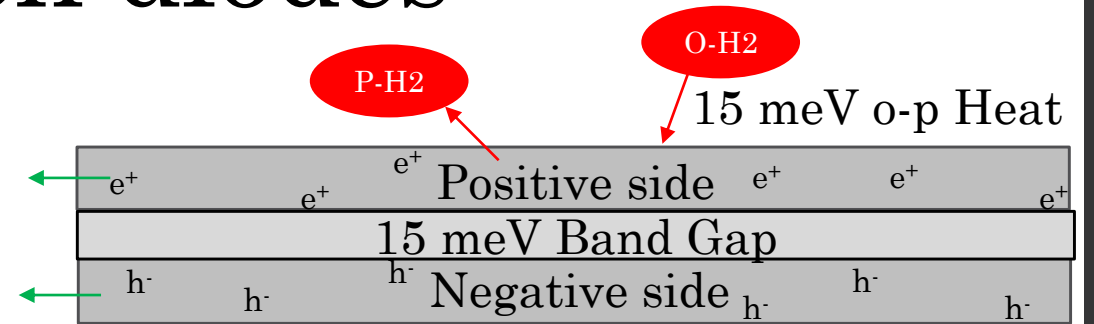
2.5 Ortho-para catalyzed regeneration

- Regenerative cycles (stirling, acoustic, pulse/GM, & magneto-caloric) tend to improve in performance (10-27%) when helium is swapped for hydrogen. (see Dros & Loftus).
- Regenerators & catalyst beds both require high surface areas, yet have never been combined.
- Regenerator scale up is challenging due to large azimuthal temperature gradients resulting in instabilities and stack by-pass. Ortho-parahydrogen conversion could counter-act stack by-pass by creating localized exotherms.
- Soundspeed differences between ortho- & para- could promote para- migration towards cold.

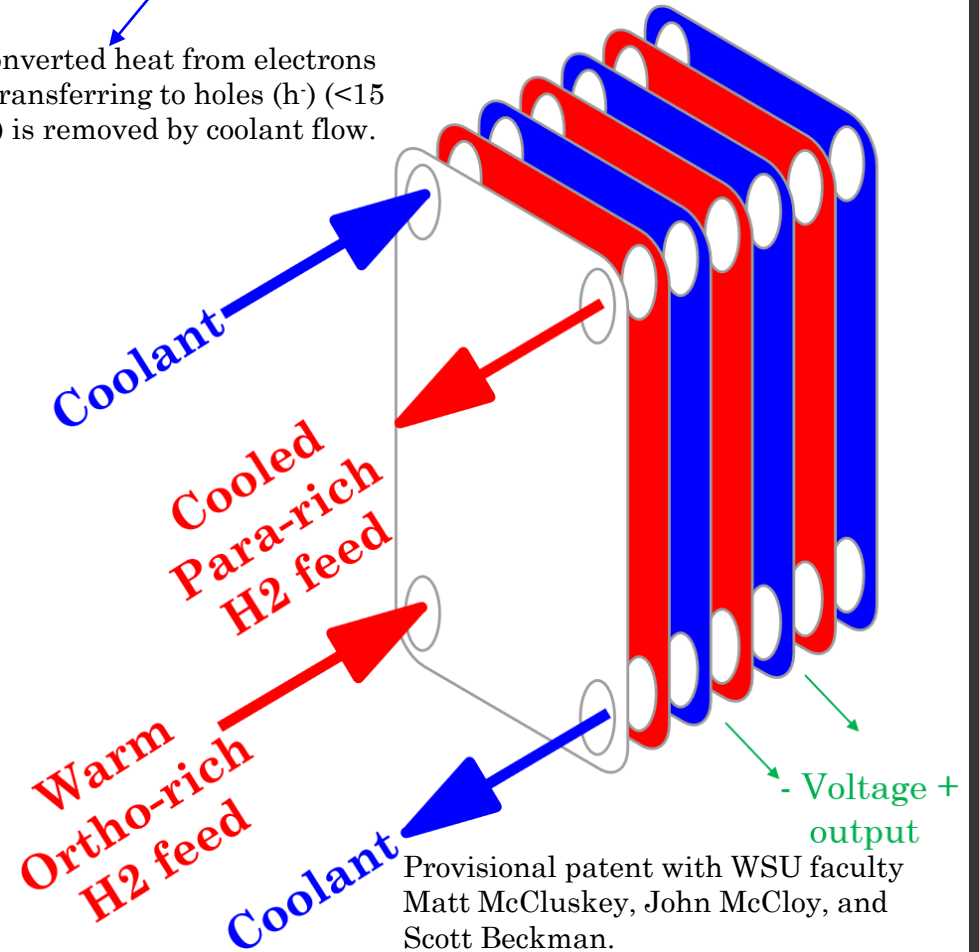


2.5 Cryogenic hydrogen diodes

- Quantized ortho-parahydrogen conversion is an opportunity for tunable phase change below 77 K.
- O-P catalysts should have high magnetic susceptibility <77 K, high surface area, and an internal energy transition matched to the conversion energy.
- P/N junction diode tuned to 15 meV turns o-p conversion heat into useful electricity.
- Reduces amount of exothermic heat lift required from any cycle (o→p) or can drive endothermic conversion for cycle cooling (p→o).
- Reduced thermal noise in cryogenics could allow higher diode efficiencies.
- In worst case could be simple ortho-parahydrogen composition sensor.



Unconverted heat from electrons (e⁺) transferring to holes (h⁻) (<15 meV) is removed by coolant flow.



Provisional patent with WSU faculty Matt McCluskey, John McCloy, and Scott Beckman.



2030 vision for hydrogen liquefaction



WSU's deployable hydrogen liquefier (photo credit Leif Harfst)

- Efficient, low-cost, 5 Tonne/day liquefier can enable:
 - Daily tanker fills,
 - Direct tanker loading,
 - Rapid tanker swapping,
 - Fits in a rocket stage,
 - Fits down the interstate,
 - Fits down an assembly line,
 - Fits in the column of a 14 MW off-shore electrolyzing wind turbine,
 - Modular+dispatchable to ramp with renewables, and
 - Opportunity to be scaled down (~500 W @ 20 K) for active cooling and zero-boil-off storage.
- Bigger only seems to get better beyond this for rotary machinery and storage spheres, not electrolyzers or transport. (Study opportunity!)
- Technology advances have always proceeded rapid capacity expansions. We will not meet our goals without fundamental technology advances.





3. LH₂ Storage

1. The First Hydrogen Bank/Tank
2. Cryogenic insulation paradigms
3. What is Vapor Cooled Shielding?
4. How can we make flexible cryogenic vessels?
5. How can we achieve ZBO through active cooling?





3.1 The hydrogen bank/tank

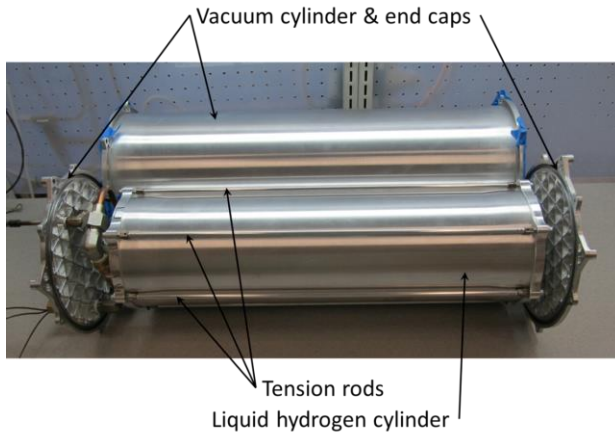
- Storing liquid hydrogen is like banking energy for later use. Only, nature requires some harsh terms & fees. Moreover, venting hydrogen could be a short-term green house gas. We need to get good at Zero-Boil-Off (ZBO) storage.

Actual Tank/Bank Specs:

- ⇒ 4300 kg LH2 capacity
- ⇒ 143 MW-hr raw energy storage
- ⇒ 1-5% per day boil off rate
- ⇒ ~500 W average heat load



3.2 Cryogenic insulation paradigms



No insulation is perfect. Each approach has pros and cons. Each of these applied alone results in the status quo: hours long transfer times & the need for external heat exchangers to prepare fuel for use.

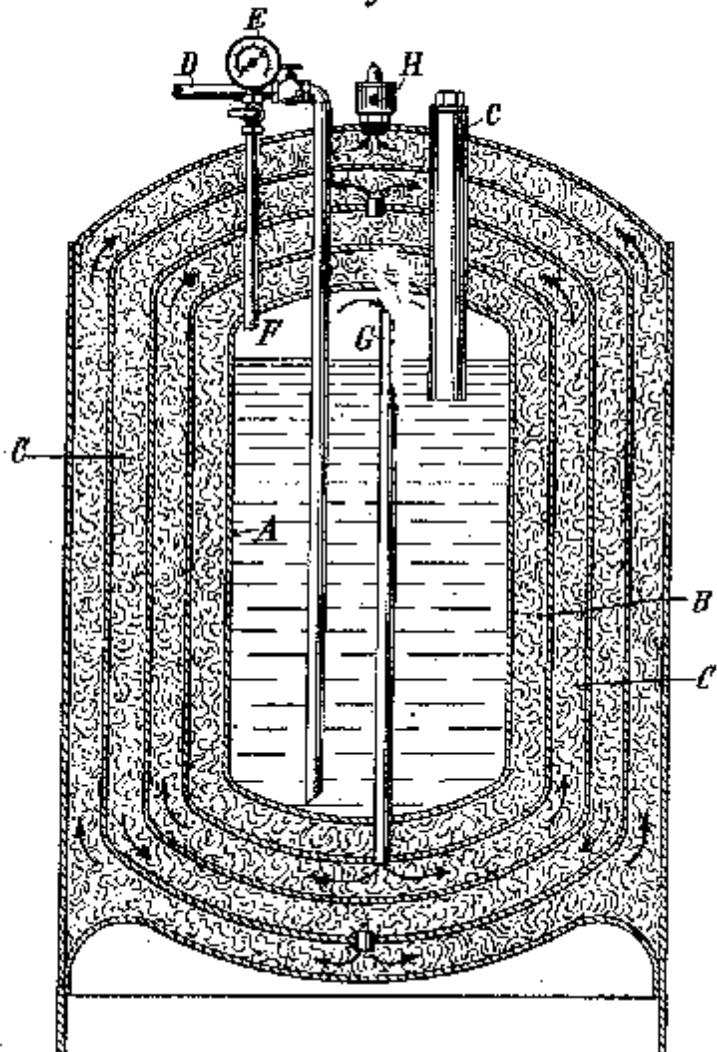
Insulation Paradigms:

1. Vacuum jacketed MLI
 - Rigid pressure vessels with 64 individually wrapped, thermally isolated, reflective film layers to minimize thermal radiation.
 - Held in a high vacuum chamber to eliminate thermal convection.
 - Suspended to eliminate thermal conduction.
 - Industry standard.
2. Spray-On Foam Insulation (SOFI)
 - 2-5 cm of polymeric foam sprayed on outside of rigid pressure vessel.
 - Lightest weight for aerospace.
3. Glass media (microbubbles & aerogels)
 - Pourable (microbubbles), rollable (aerogels), reflective, convection disrupting, non-settling.
 - Cost is improving with scale.
 - Could become best choice for manufacturability and field use.



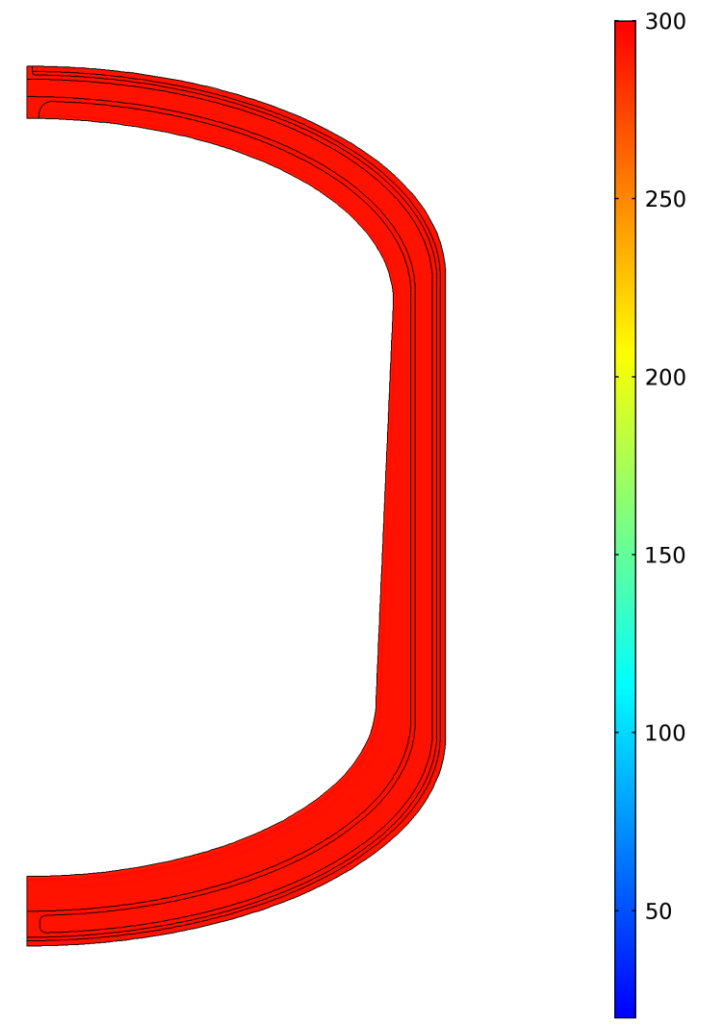
3.3 Vapor Cooled Shielding (VCS)

Fig. 1



- Vapor cooled shielding has long been established technology.
- Utilizes the stored thermal energy of the cryogen to shield or intercept the incoming heat.
- 4300 kg LH2 tanker had a heat load of 500 W, the hydrogen boil off at that heat load can lift 7800 W of heat. Clearly VCS can be a key advance for cryogen storage.
- Difficulty has always been manufacturability.

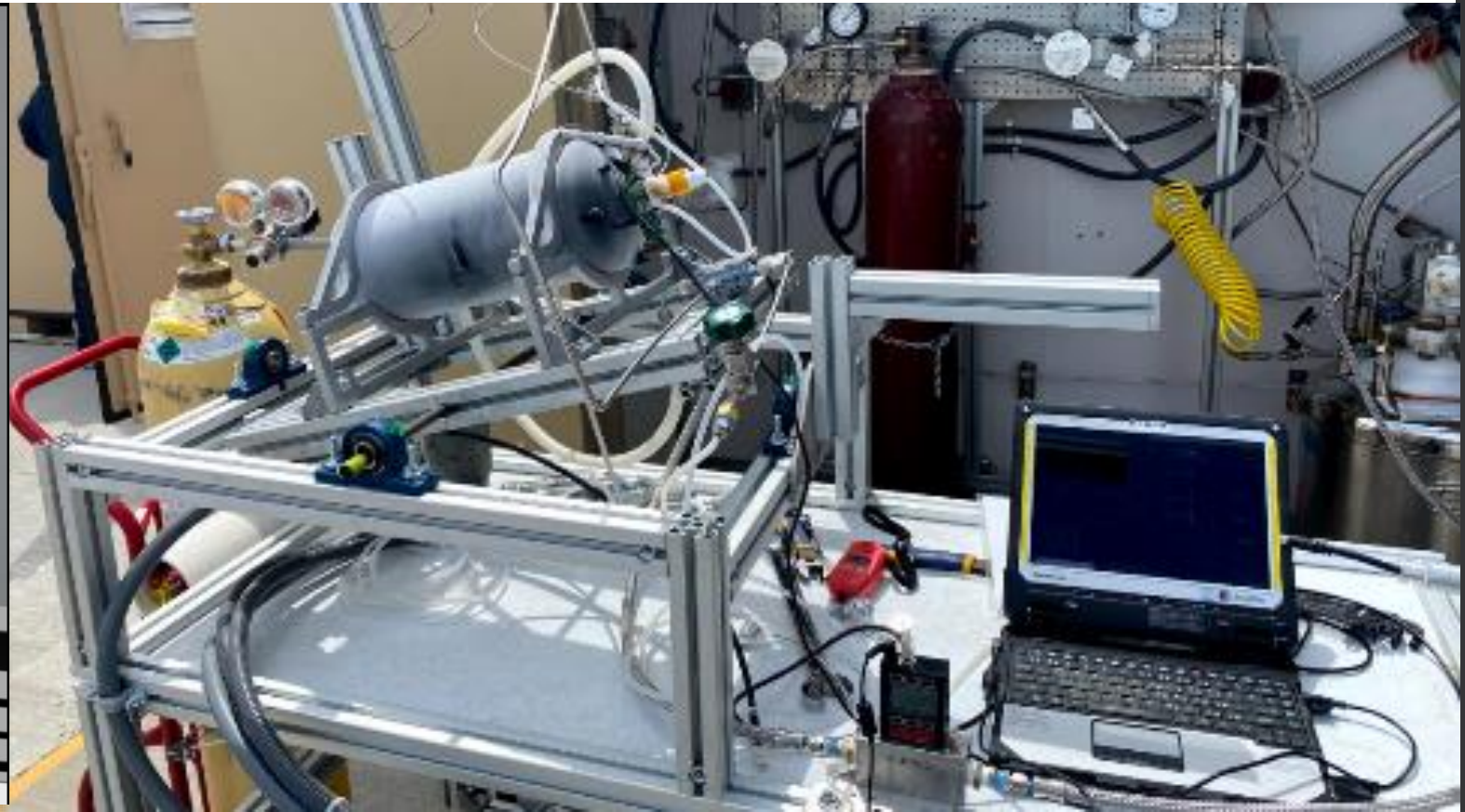
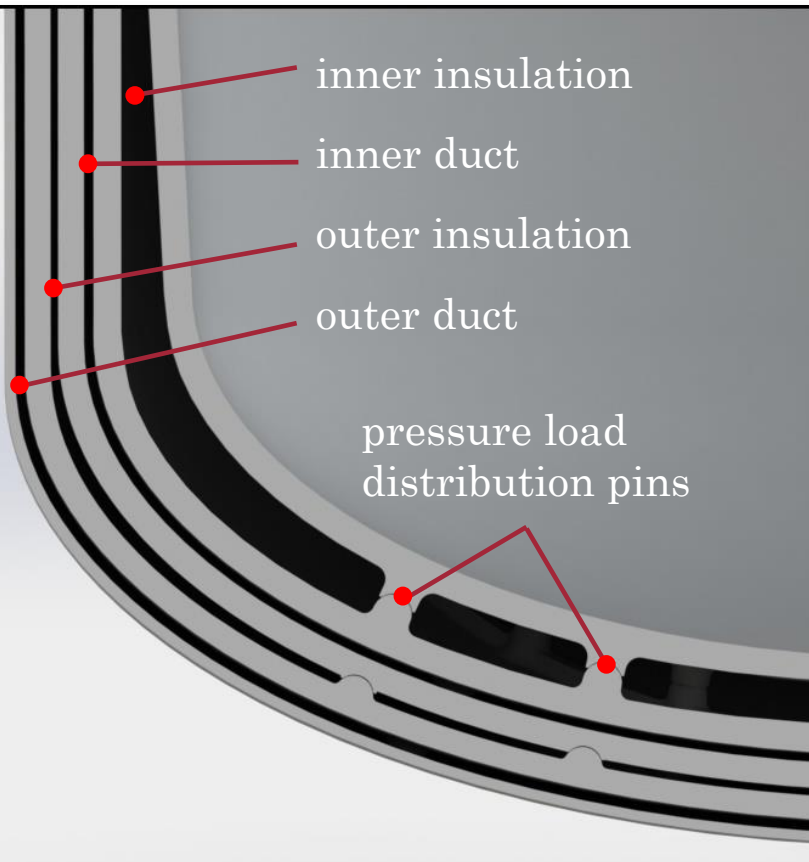
Time=0.01 s Surface: Temperature (K)





3.3 3D printed vapor cooled shielding

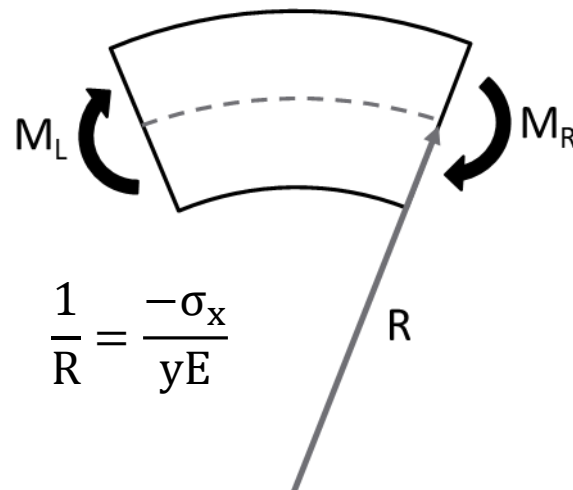
- Developed liquid hydrogen VCS tanks for use on robotic vehicles.
- Tested boil off during roll/pitch.
- Completed over 50 fills, 10 min fill time typical, 5 min fast fill, 15% mass fraction H₂.



3.4 How to make flexible cryo tanks



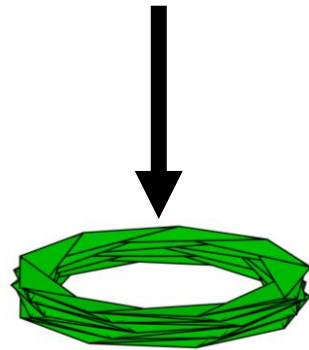
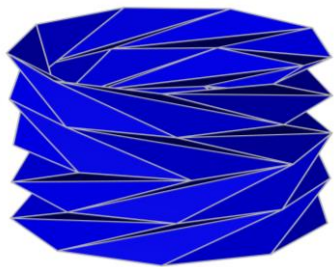
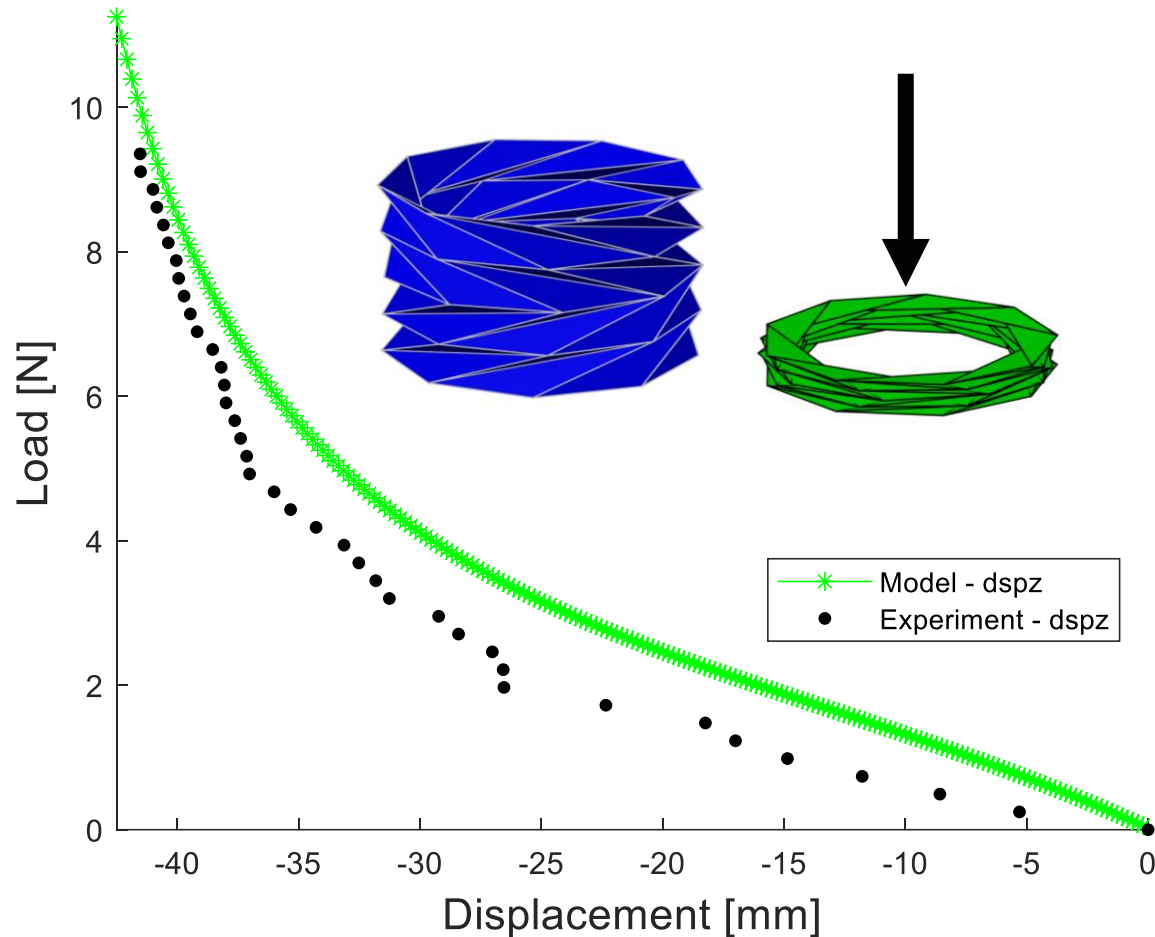
- Permeation testing of thin films at liquid hydrogen temperatures led to a need to understand the failure mechanisms of fuel bladders.
- With a minimum Young's modulus, the seams of the bellows form a living hinge that flexes with a radii that allows bulk deformation without failure.
- We're now vacuum forming bellows.





3.4 Cryogenic origami fuel bladders

- Thin films can act as living hinges to flex thousands of cycles even at cryogenic temperatures. Video on right is a vacuum formed polycarbonate film in liquid nitrogen. 1x speed.



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3.5 ZBO via active cooling

- We need ~ 500 W to achieve ZBO.
- The biggest pulse-tube cryocoolers only achieve ~ 50 Watts of cooling at 20 K.
- Some Stirling coolers can achieve ~ 200 Watts at 20 K, with a 45 kW input.
- We need more efficient large-scale coolers in the 500 W range as turbo cycles do not scale down well.

• 23.8 kW of electrical power is required to run a 30% exergetic efficient cooler to lift 500 W. This power could easily come from a solar panel mounted over a storage tanker, or from the hydrogen boil-off from the tank and a fuel cell.





2030 vision for ZBO LH₂ storage



- Cryogenic origami fuel bladders can be a new generation of ZBO liquid hydrogen tanks:
 - Theoretical optimum mass fraction of LH₂
 - Eliminates risk of ullage collapse
 - Multi-wall bladders allow minimum-cost vapor shielding and active cooling
 - Potentially minimum manufacturing cost if vacuum formed
- Active coolers can be developed to work autonomously with solar and fuel cell power to achieve ZBO, even from traditional tanks.
- More research is needed to characterize 3D printed materials and specifically polymers at these conditions.

NASA's opportunity:



Develop the next generation of LH₂ technologies for both renewable energy & spacecraft. With common form factor, modularity, autonomy, and efficiency needs, these hydrogen liquefiers + ZBO storage systems can ensure Humanity's continued evolution across the Solar System.





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School of Mechanical and Materials Engineering ↗

Voiland College of Engineering and Architecture ↗

WSU Safety



Cool. Fuel.

The only cryogenic hydrogen research laboratory in US academia.

Innovating electrofuels since 2010.



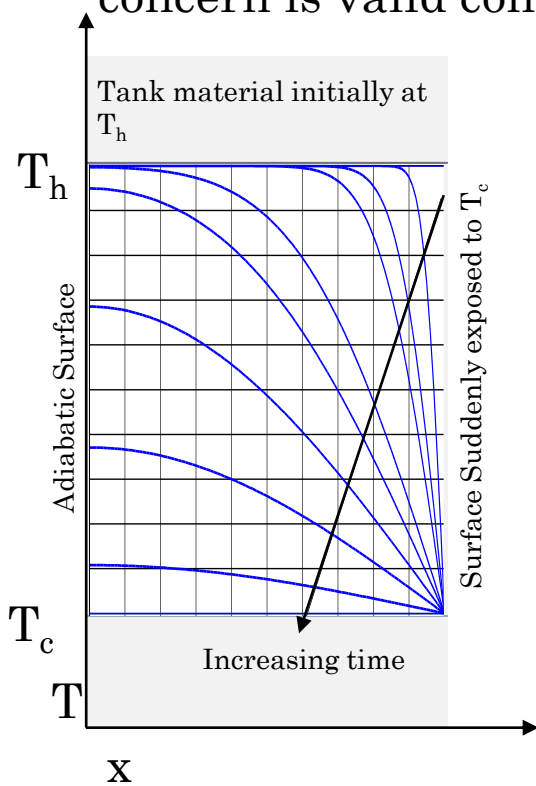
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<https://hydrogen.wsu.edu/>



3.2: Insulation thermal response time

Context: You've come up with a novel design for a lightweight polymer tank design. But an expert is concerned about the low thermal response time. The concern is valid considering:



Thermal Penetration length

$$\delta_i = 2\sqrt{\alpha t}$$

Thermal Diffusion Time Constant

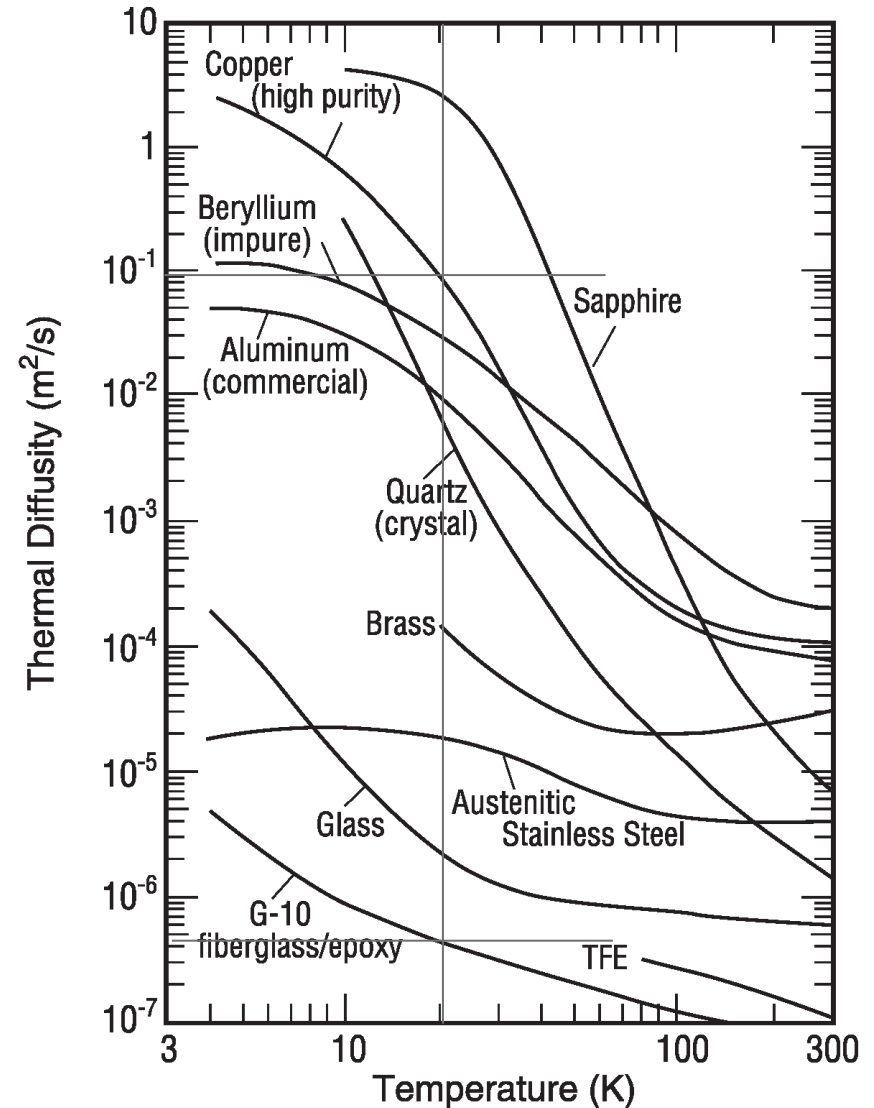
$$\tau_{diff} = \frac{L^2}{4\alpha}$$

A 1 second response time for copper becomes a 13.8 hour response for plastics!

Question: Estimate the thermal response time for a 4 mm thick polymer shell at 20 K.

Solution: $0.004^2 / (4 * 3E^{-7}) = 13.3 \text{ s}$ (not horrible)

G. Nellis & S. Klein, "Heat Transfer" Cambridge 2010



J. Ekin, "Experimental Techniques for Low Temperature Measurements" Oxford 2006

3.3 Vapor cooled shielding extraction

- Tanks can be designed to extract highest entropy vapor from ullage space.
- Para-orthohydrogen conversion can further increase entropy extraction and result in the need for less mass extraction (or venting) to maintain tank pressure.
- If ullage space is at 94 K, para-orthohydrogen conversion can increase cooling capacity of flow by 50%. Only 0.35 g/s of hydrogen venting is enough to lift the 500 W heat load.

