Hydrogen: Novel Liquefiers for Novel Molecules

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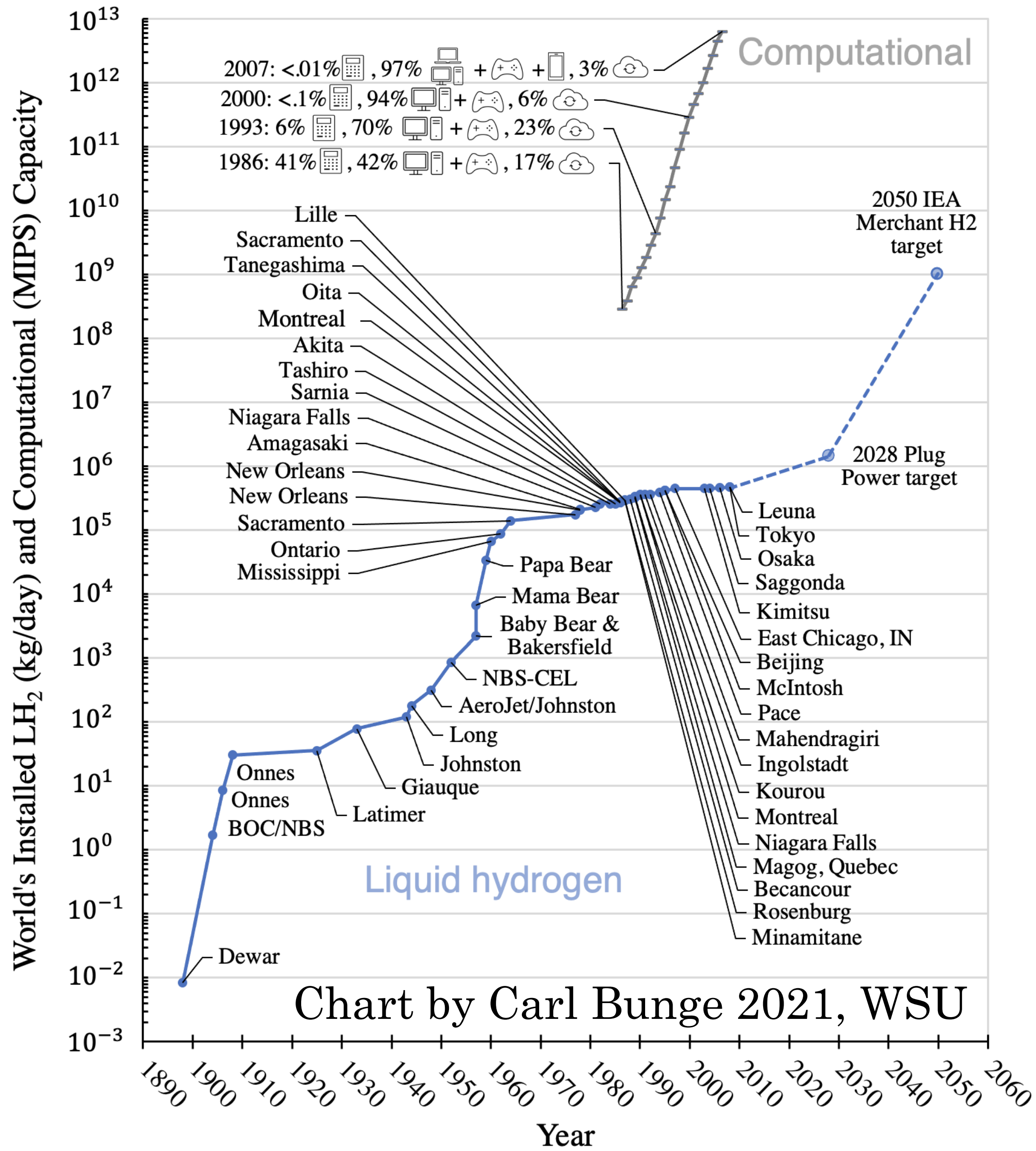
Cool. Fuel.

In this talk:

1. H_2 fundamentals.
2. Liquefaction basics.
3. Emerging concepts.

2030 Vision: 5 T/day, modular, dispatchable



- Efficient, low-cost, 5 Tonne/day liquefier enables:
  - 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.

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1. H_2 fundamentals.

1. Novel hydrogen physics: quantum swelling
2. Novel hydrogen physics: nuclear spin isomers
3. Ideal-gas property effects

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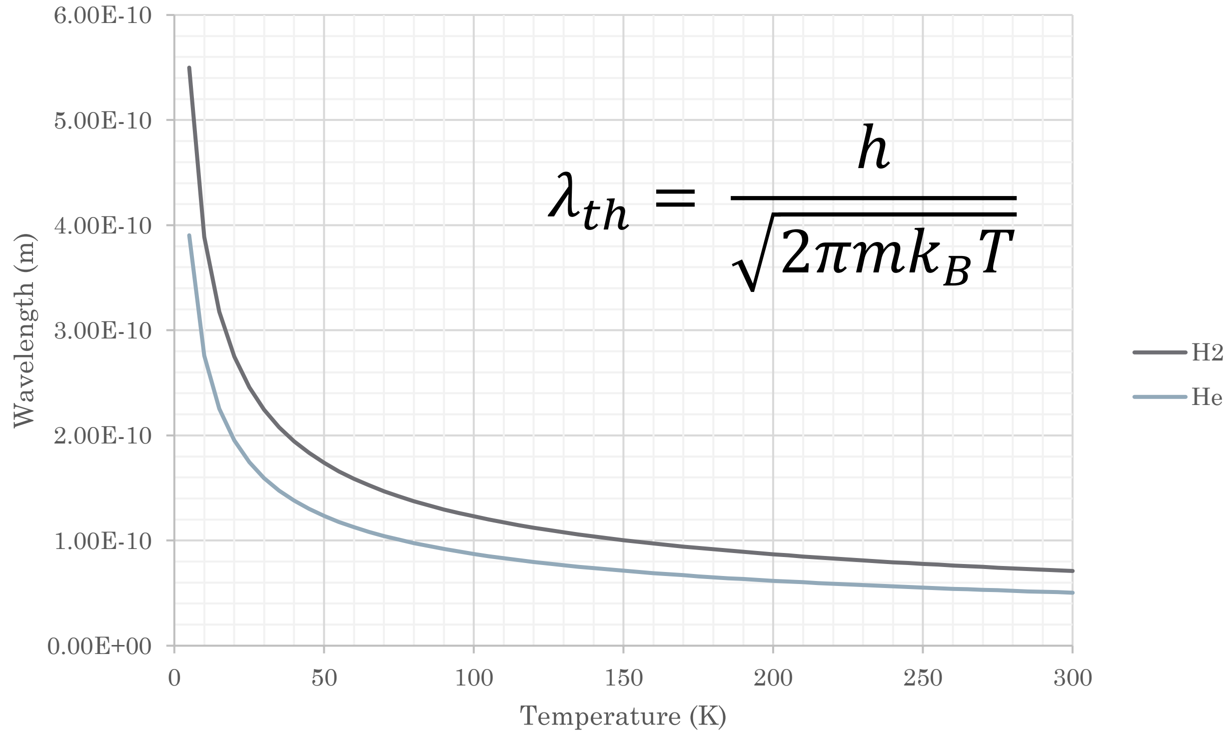
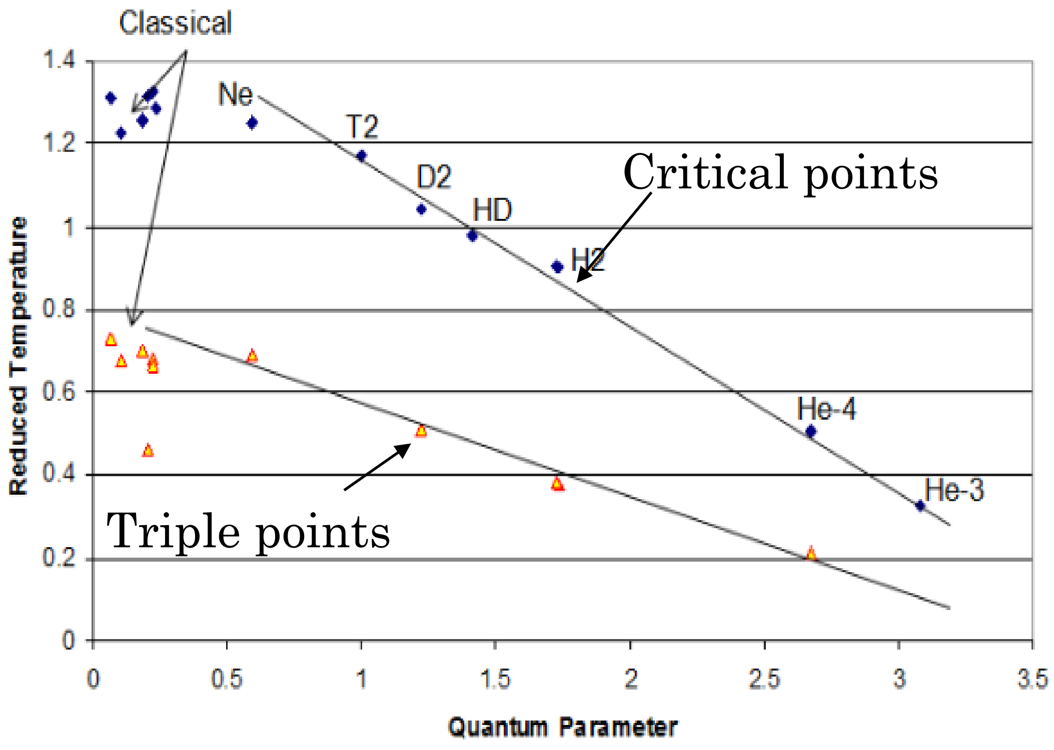
1.1 Novel H_2 Physics: Quantum Swelling

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



$$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$$

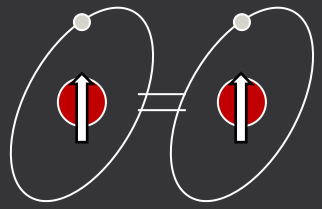


1.2 Novel H_2 Physics: Nuclear-Spin Isomers

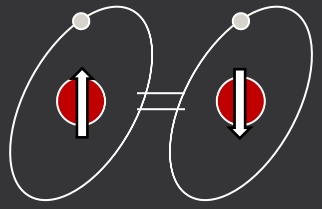
In 1932, Werner Heisenberg won the Nobel Prize:

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

[1]Nobelprize.org accessed 2010



Normal Hydrogen 3:1



Orthohydrogen

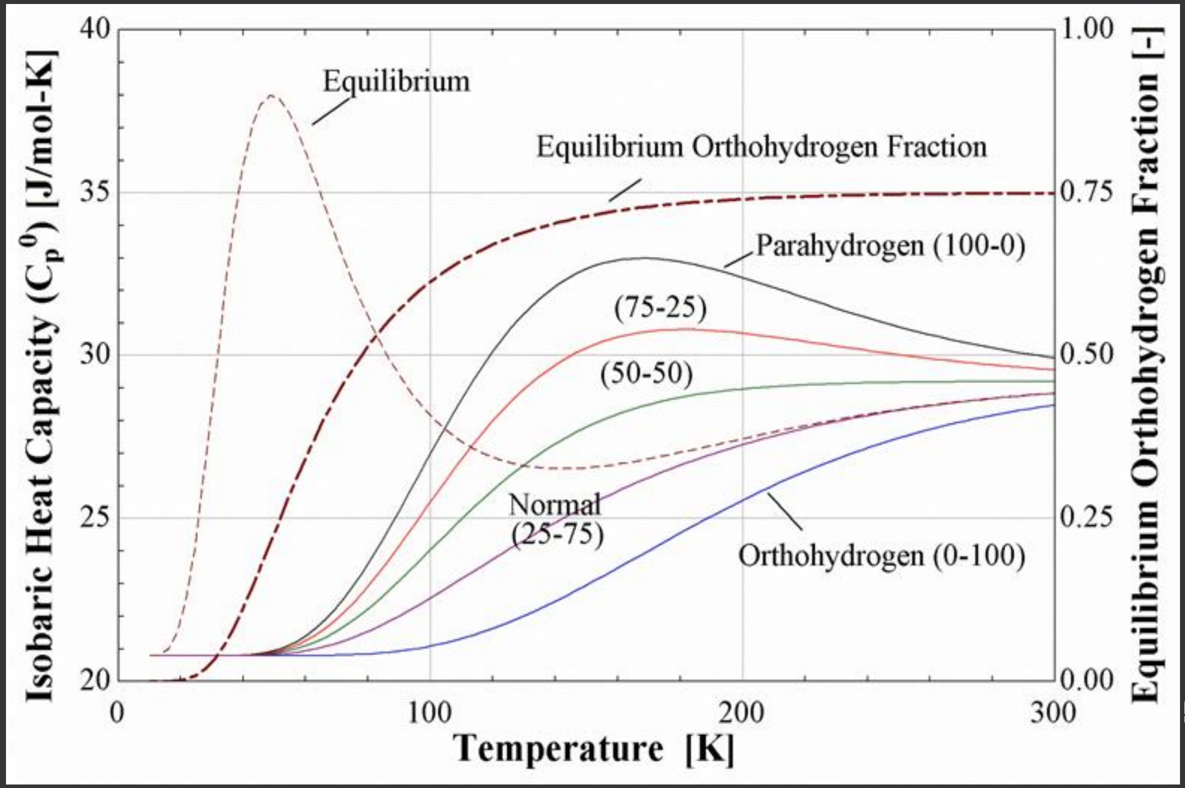
$$\underset{(antisym)}{\psi_{tot}} = \underset{(sym)}{\psi_{vib}} \underset{(antisym)}{\psi_{rot}} \underset{(sym)}{\psi_{spin}}$$

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

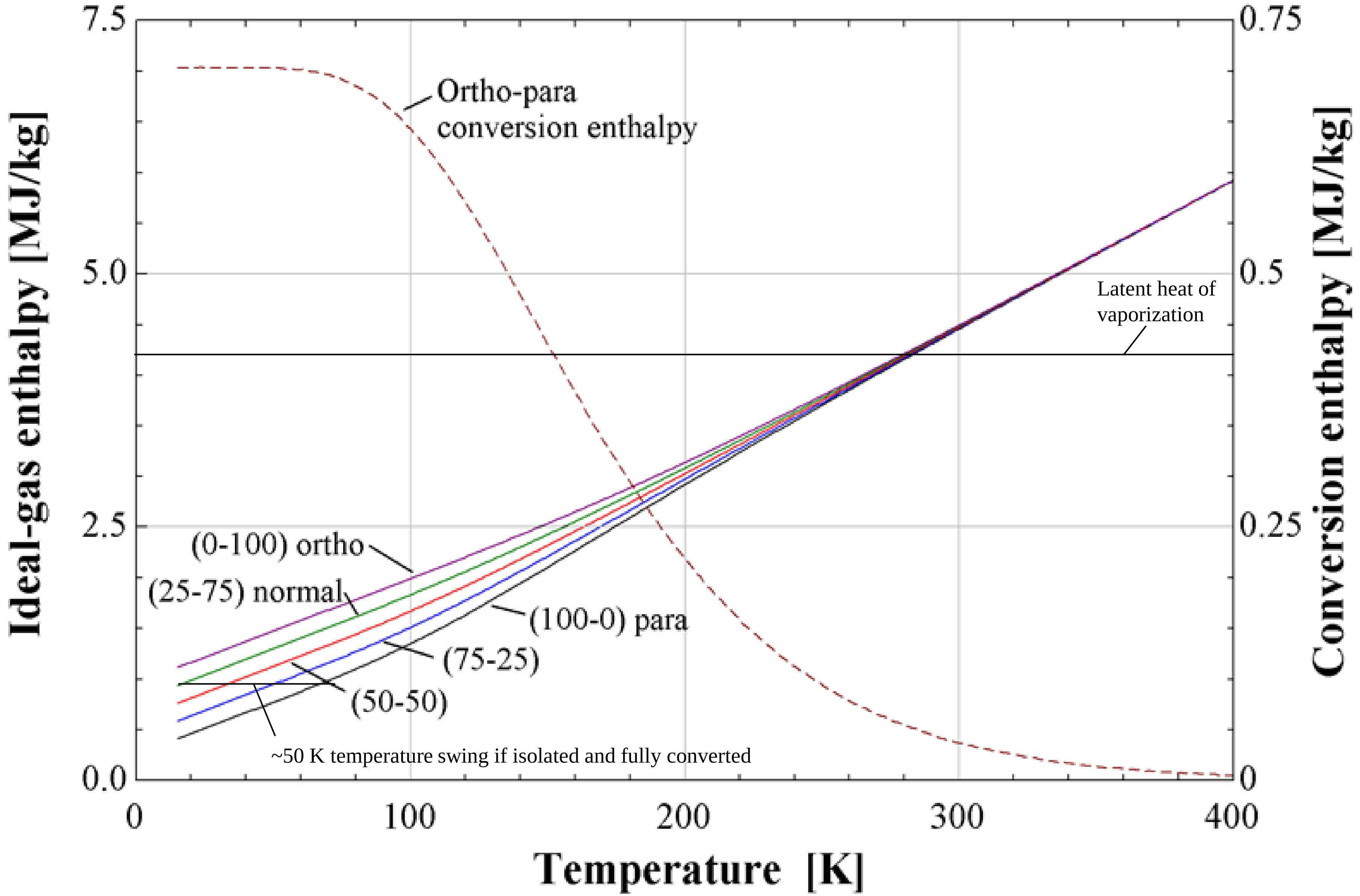
Parahydrogen

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

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



1.3 Ortho-para effects on properties: Enthalpy



2. Liquefaction Basics.

1. Hydrogen liquefier efficiencies
2. Fundamentals of refrigeration
3. Opportunities: change the input
4. Opportunities: change the entropy
5. Opportunities: change the enthalpy
6. Opportunities: change the output

2.1 Hydrogen liquefier efficiencies

- 1st Law Efficiency

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

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

- Carnot (ideal) Efficiency

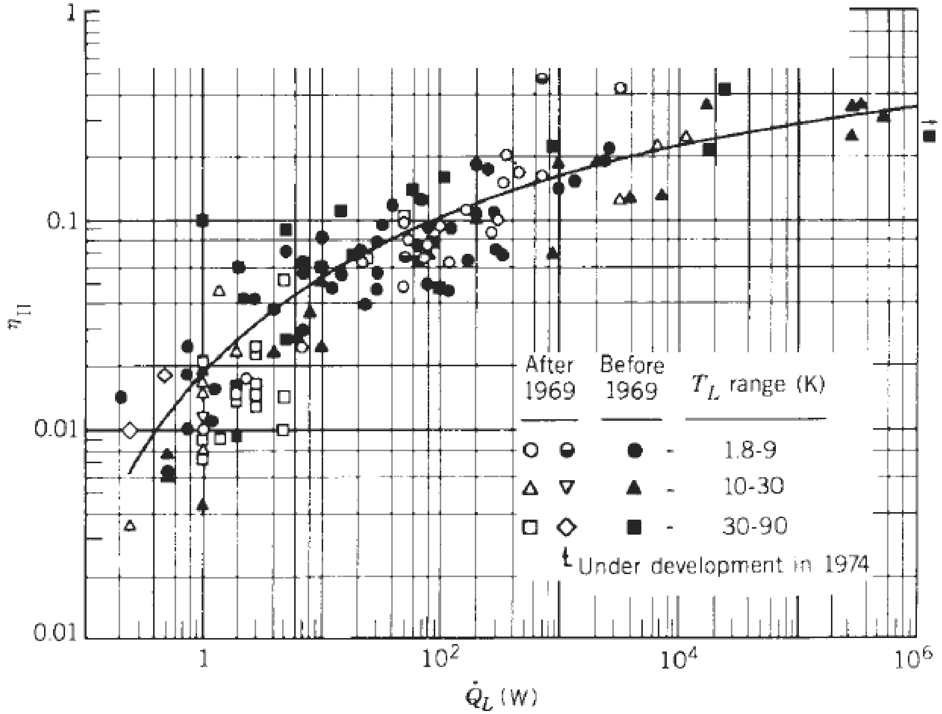
$$COP_C = \frac{T_C}{(T_H - T_C)}$$

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

- 2nd Law (exergetic) Efficiency

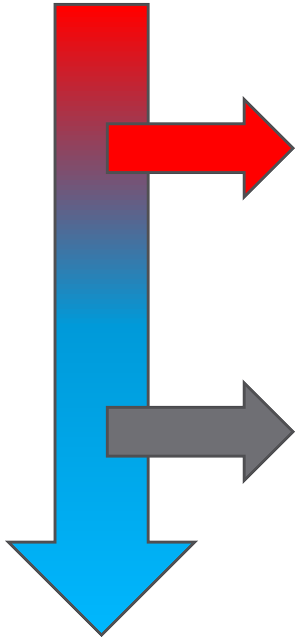
$$COP_{II} = \frac{Best\ you\ could've}{How\ you\ did} = \frac{COP_C}{COP_I}$$

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



2.2 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

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

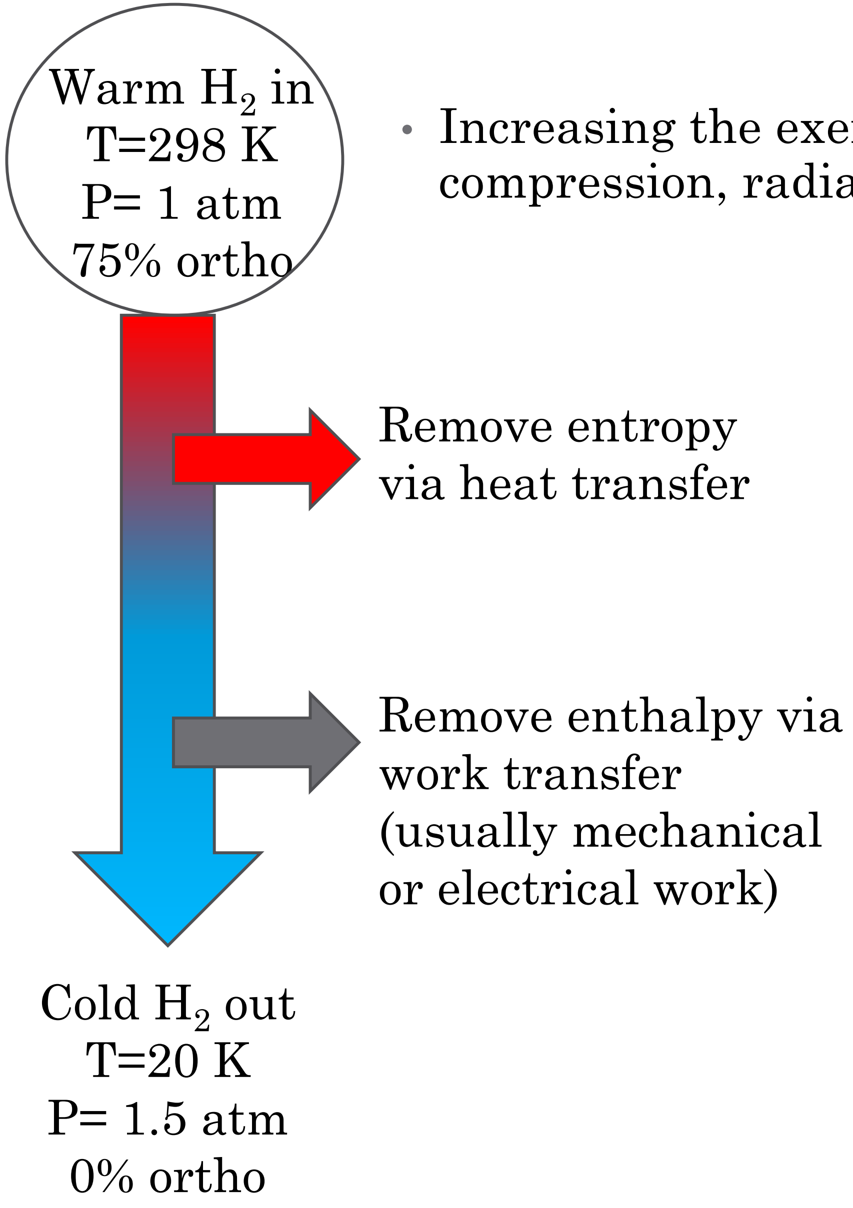
$(h - h_0)$: 4428 kJ/kg

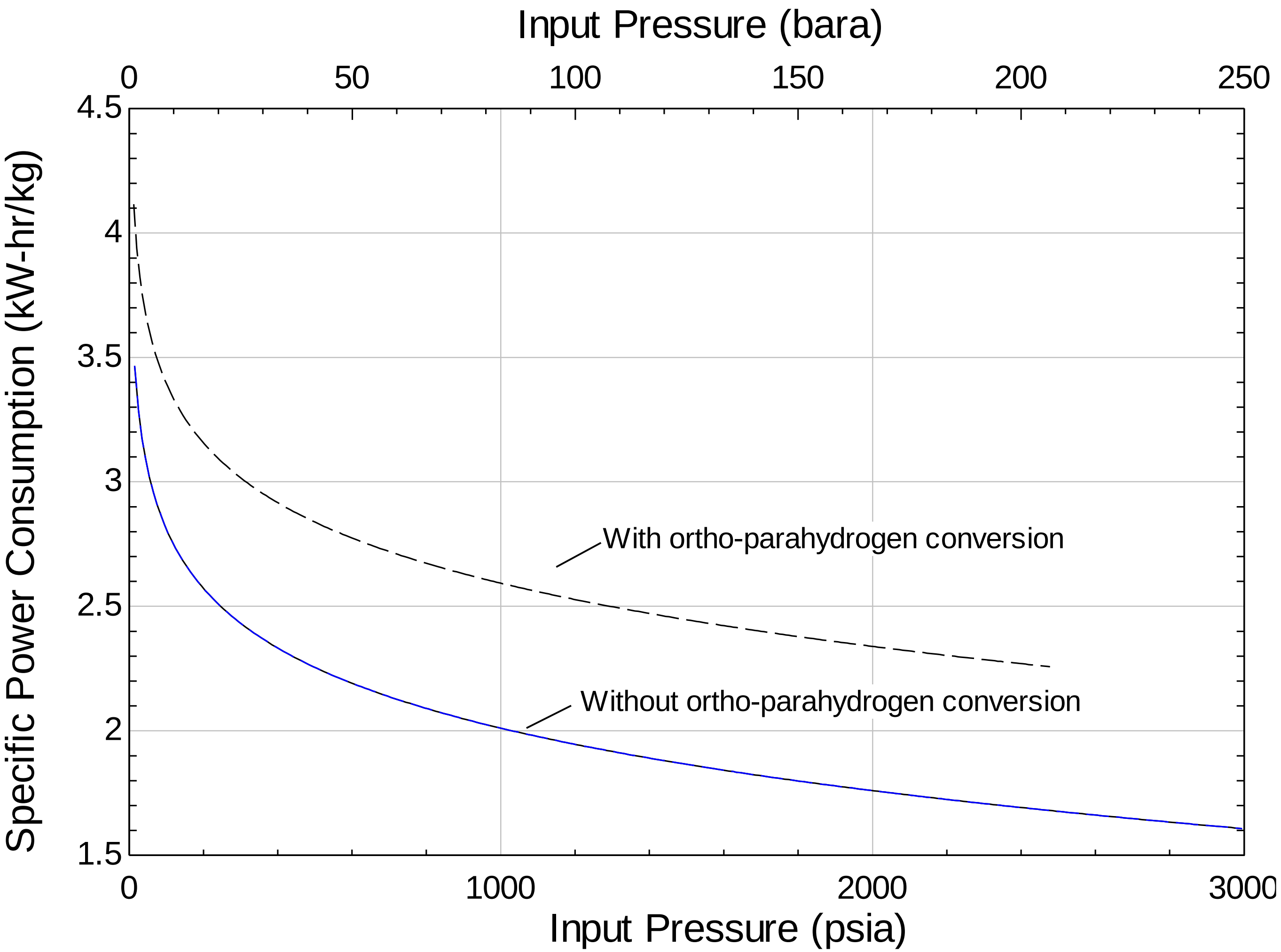
$T_0(s - s_0)$: 16921 kJ/kg

Entropy contribution to exergy is 4x the enthalpy.

2.3 Opportunities: change the input

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





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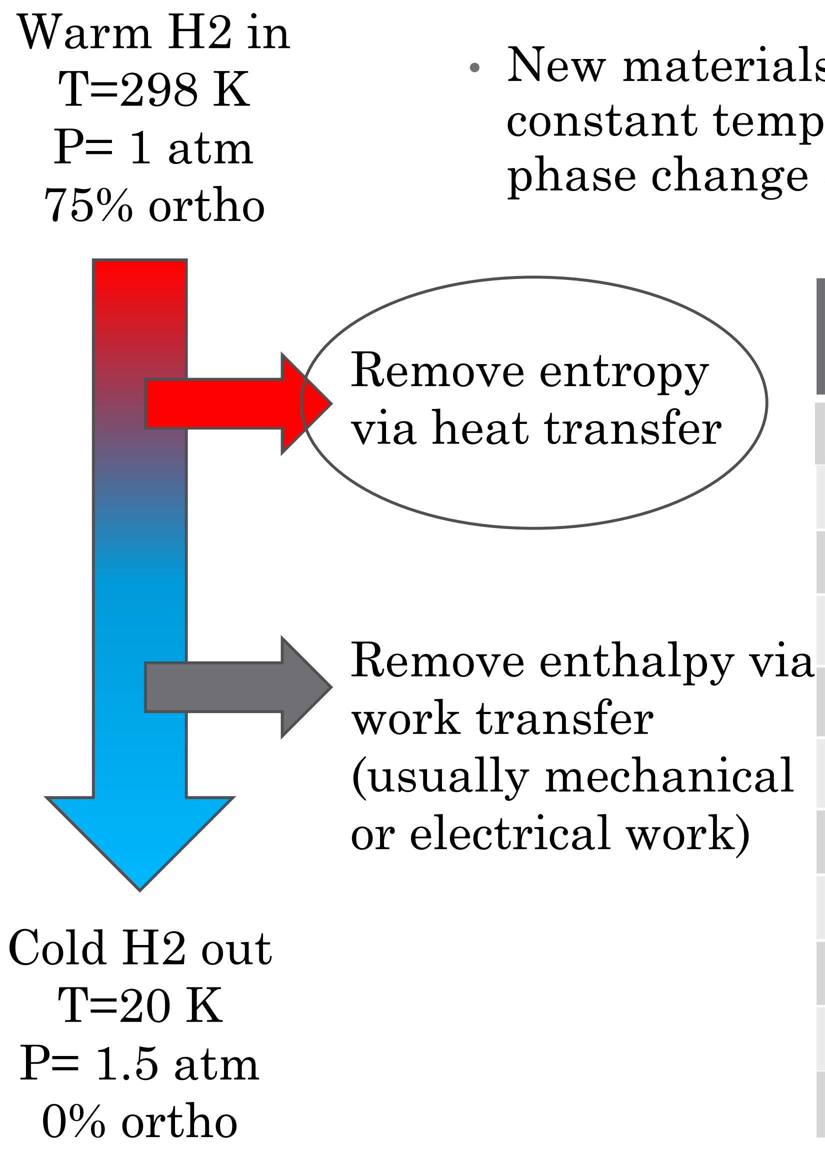
2.4 Opportunities: change the entropy

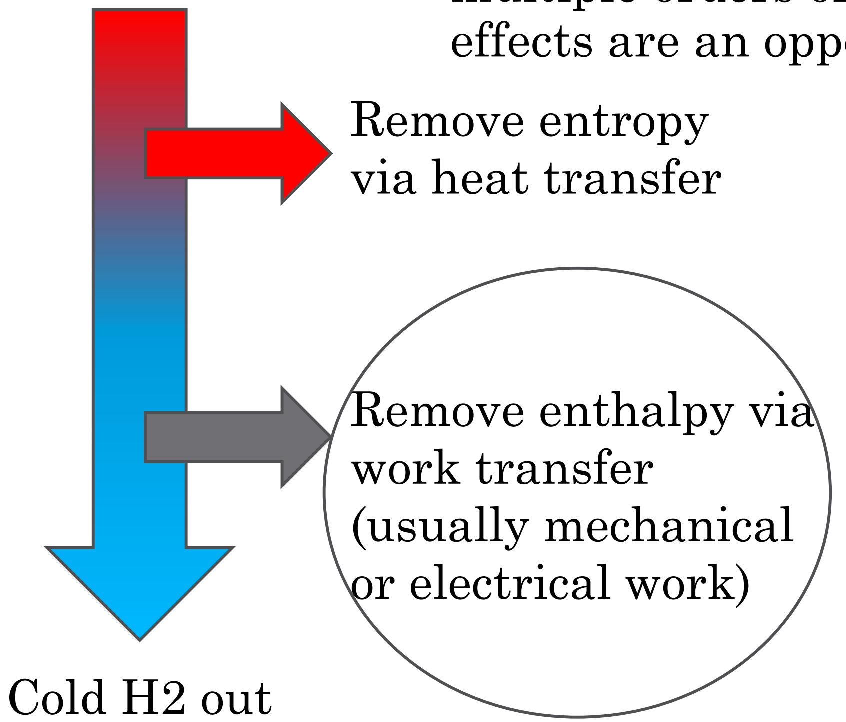


- New materials are being created that allow for changes in entropy at constant temperature (phase change). Ability to control phase change, and phase change size are what controls the efficacy.

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

2.5 Opportunities: change the enthalpy

- 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.



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

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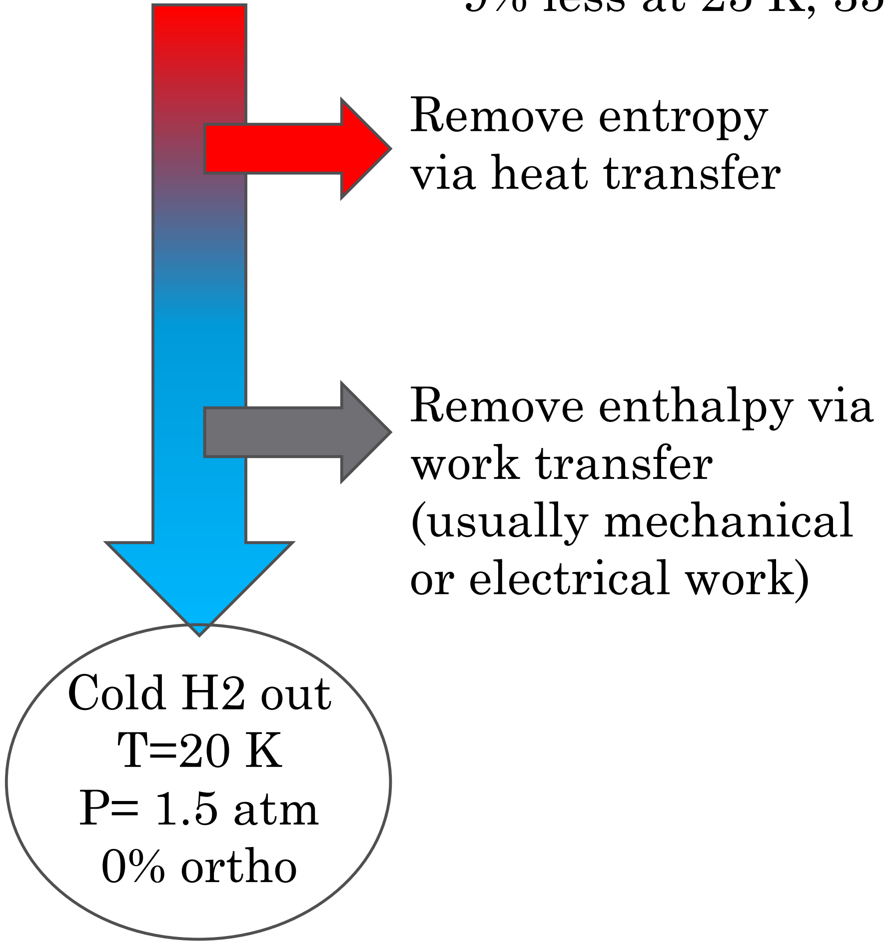
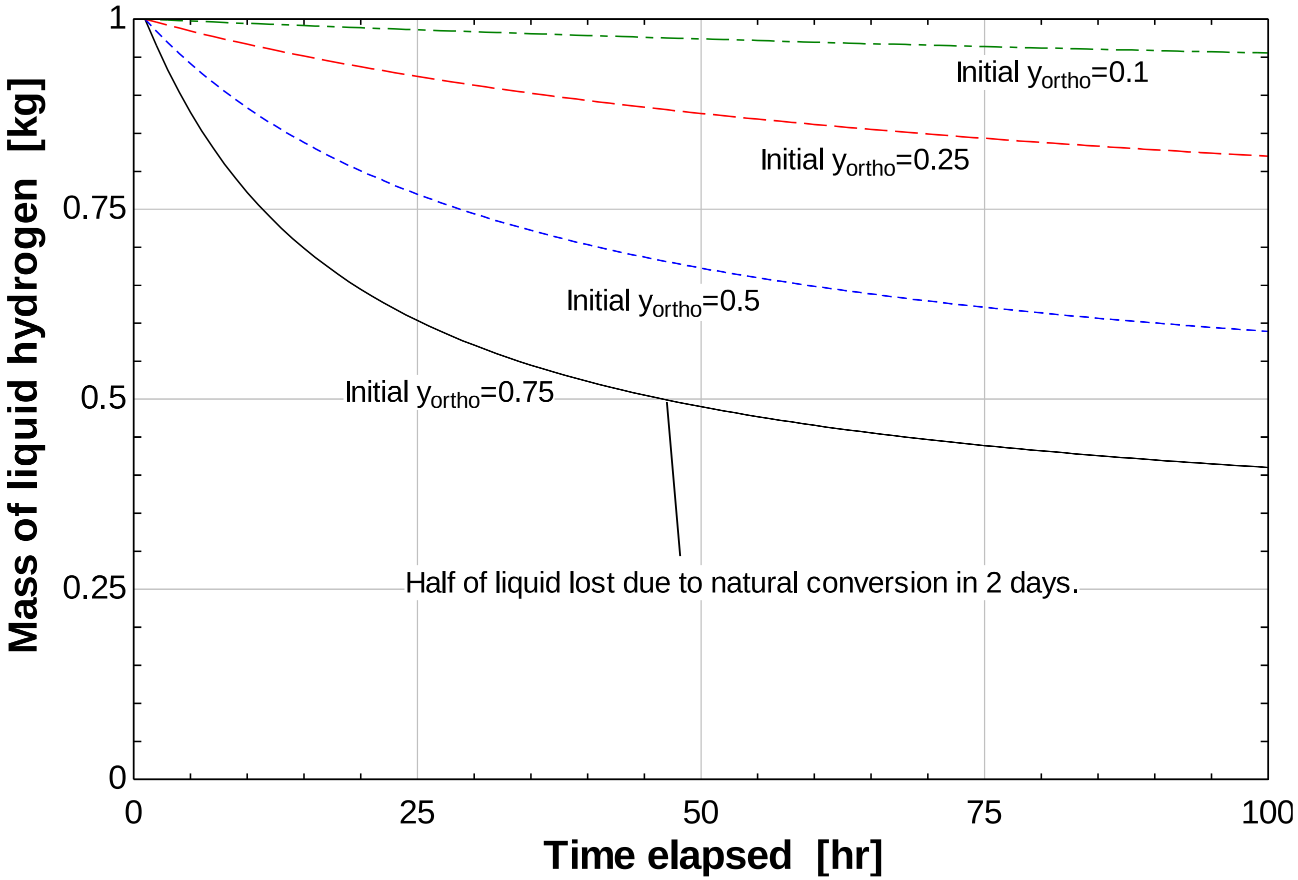
2.6 Opportunities: change the output

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.



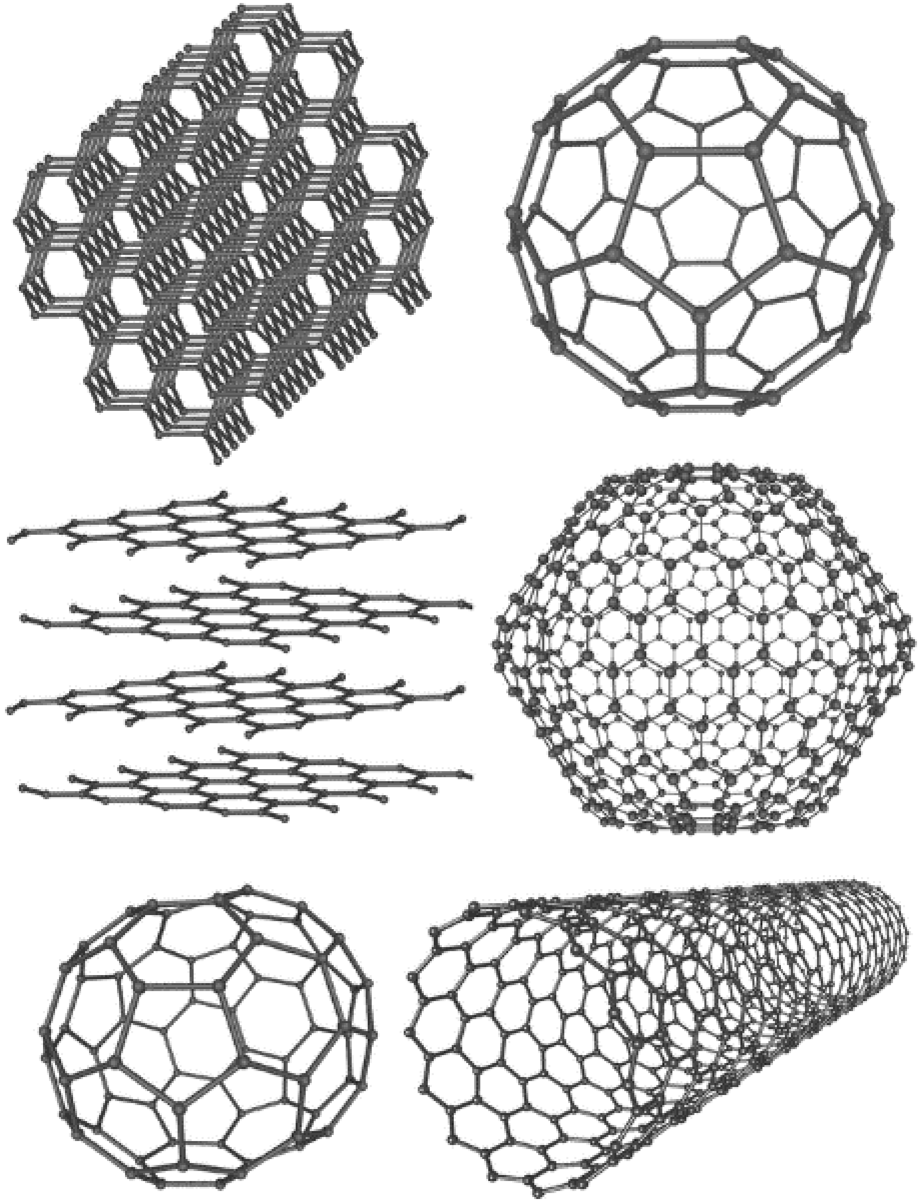


3. Emerging Concepts.

1. Quantum plumbing
2. Ortho-parahydrogen catalyzed regeneration
3. Cryogenic hydrogen diodes

3.1 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.



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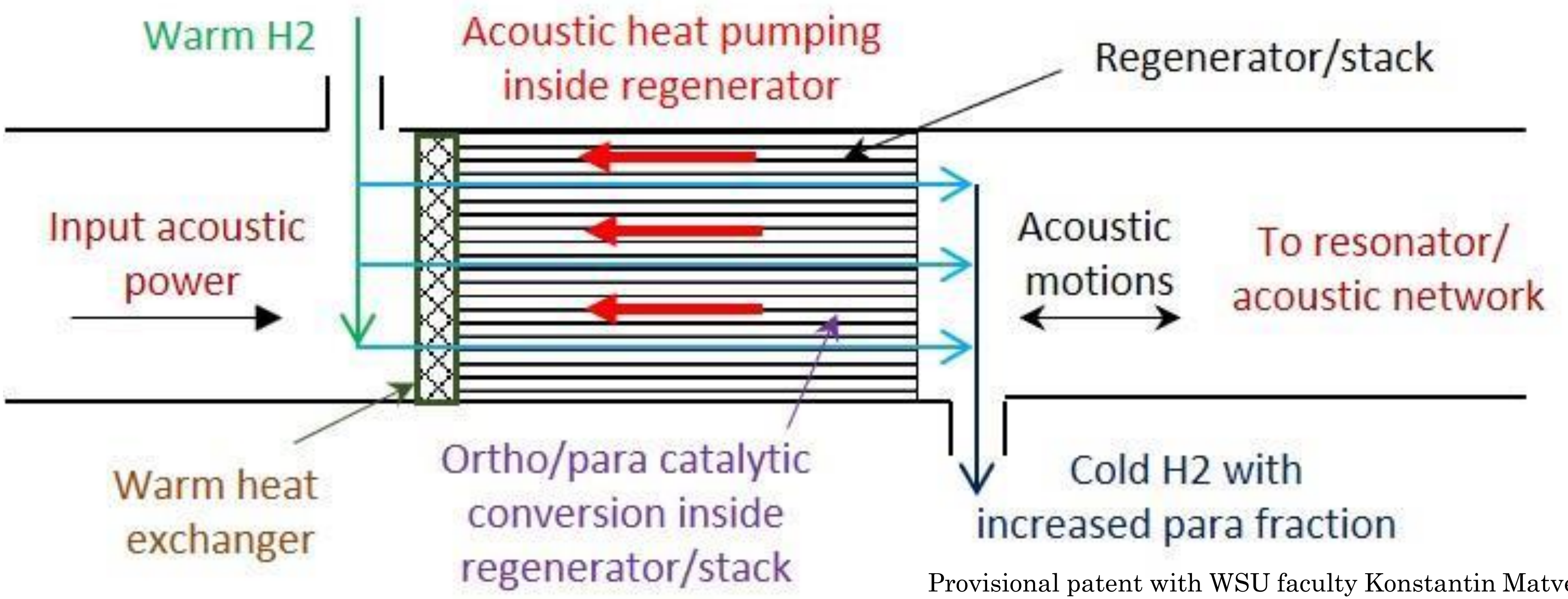
3.2 Ortho-para catalyzed regeneration

- 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.



Provisional patent with WSU faculty Konstantin Matveev

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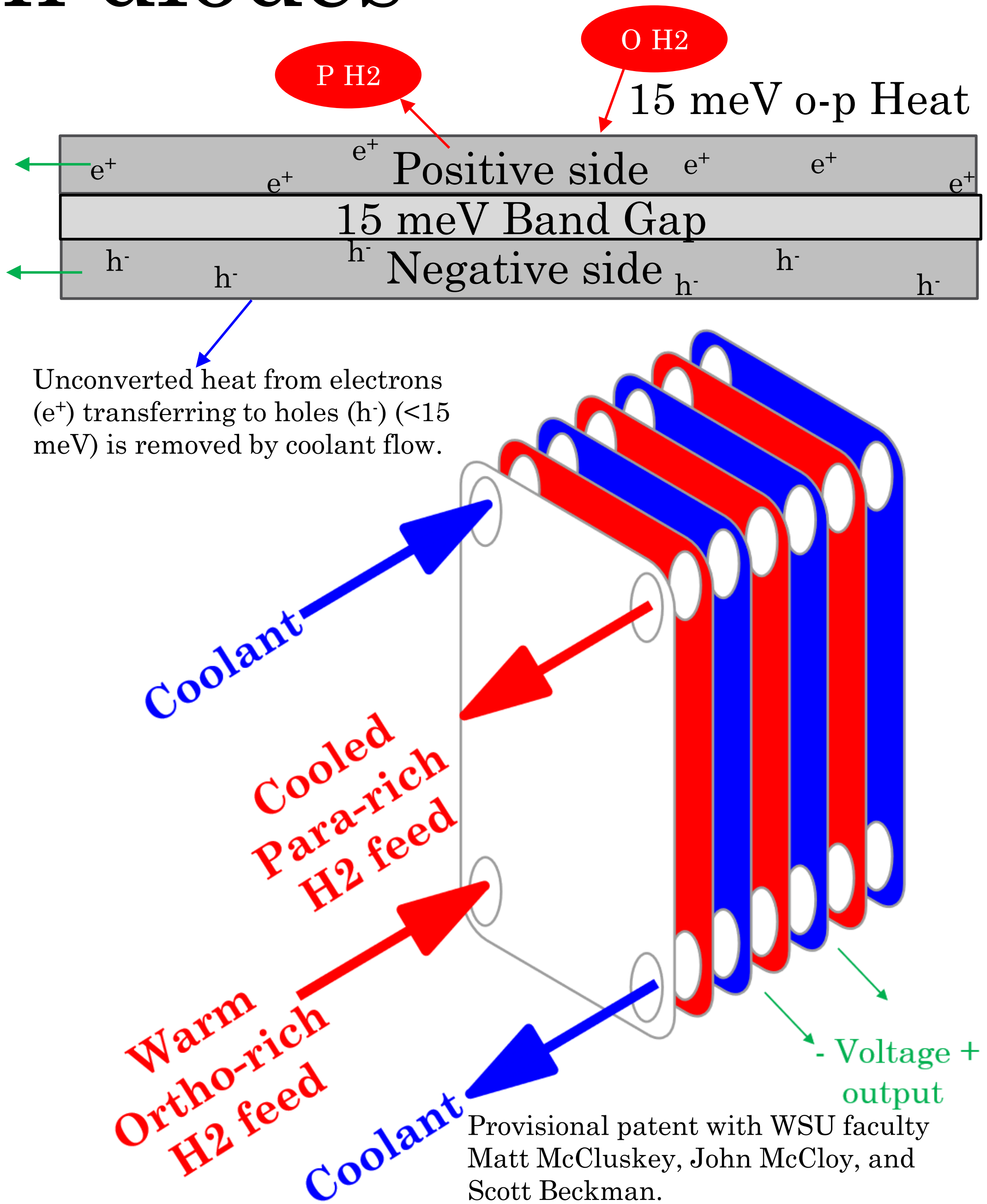
3.3 Cryogenic hydrogen diodes

- 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.



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

4. In Summary.

1. We need many 5 T/day, efficient, low-cost liquefiers, and fast.
2. Cryogenic hydrogen liquefier concepts have not addressed this need, let alone advanced, in 50 years.
3. Hydrogen has unique quantum opportunities for liquefiers.
4. Several quantum concepts have the potential to advance nearly all LH2 cycles; but more fundamental research is needed, now.

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Thank You!

Please, follow along, reach out, or visit for a tour:
https://hydrogen.wsu.edu/; Jacob.Leachman@wsu.edu; @hydrogenprof

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