Liquefaction of “Permanent” Gases

Hydrogen as an example

See Flynn Ch. 3 and 6

Liquefaction of Hydrogen

- Heat of Normal-to-Para conversion
- TS diagram for a pure substance
- Milestones in hydrogen liquefaction
- Liquid hydrogen production in the last 40 years
- Hydrogen liquefaction plants in North America
- Economics of liquefaction
- Four things that can be done to a gas
- Gas Liquefaction cycle temperature/Entropy diagram
- Liquefier block diagram
- Linde cycle
- Temperature/Entropy diagram
- Inversion curve for various gases
- Linde Cycle with pre-cooling
- Claude Cycle
- Ideal Liquefaction and other cycles
- Ortho-Para conversion Mechanics
- Areas of possible improvement
- Compressing hydrogen

Liquid Hydrogen

- Liquid hydrogen has the highest storage density of any method
- But it also requires an insulated storage container and energy-intensive liquefaction process
- Liquefaction is done by cooling a gas to form a liquid.
- Liquefaction processes use a combination of compressors, heat exchangers, expansion engines, and throttle valves to achieve the desired cooling

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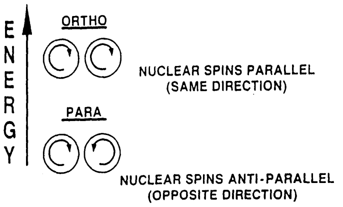
Two forms of hydrogen molecule



ΔE=171 K
<300 K

Normal H_2 (300 K and 1 atmosphere) is 75% ortho 3 quantum states
25% para 1 quantum state

Liquid H_2 (20.4 K and 1 atm.) is almost 100% para (T_{boil}<<171 K)

Heat of conversion o $\Rightarrow$ p = 0.15 kWh/kg
Heat of liquefaction = 0.12 kWh/kg
} more energy to convert than liquefy

Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 128

Ortho-Para conversion

- Hydrogen molecules exist in two forms, Para and Ortho, depending on the electron configurations
- At hydrogen’s boiling point of 20 K(-423°F), the equilibrium concentration is almost all Para-hydrogen
- But at room temperature or higher the equilibrium concentration is 25% Para-hydrogen and 75% Ortho-hydrogen
- Uncatalyzed conversion from Ortho to Para-hydrogen proceeds very slowly
- Ortho to Para-hydrogen conversion releases a significant amount of heat (527 kJ/kg [227 Btu/lb])

Percent para H_2 vs. Temperature

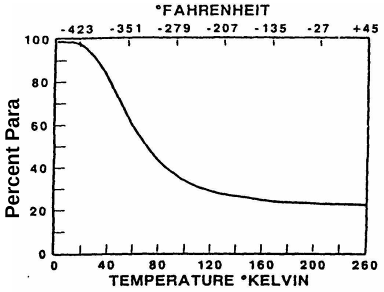


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 129

We will find that continuous conversion during liquefaction is most efficient, but capital intensive

Heat of Normal-to-Para conversion

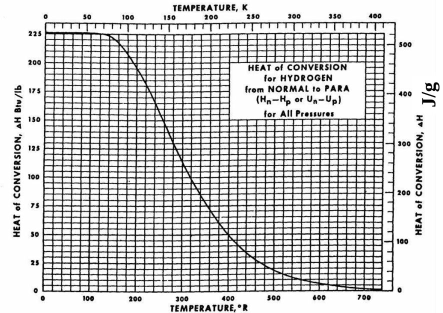


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 137

Remember, normal hydrogen is at 300 K (RT). Clearly we need to concern ourselves with catalyzing the ortho-para conversion

Ortho-Para conversion Mechanics

- Activated charcoal is used most commonly, but ferric oxide is also an inexpensive alternative
- The heat released in the conversion is usually removed by cooling the reaction with liquid nitrogen, then liquid hydrogen.
- Liquid nitrogen is used first because it requires less energy to liquefy than hydrogen, achieving an equilibrium concentration of roughly 60% Para-hydrogen

Ortho-Para conversion notes

- If Ortho-hydrogen remains after liquefaction, heat of transformation described previously will slowly be released as the conversion proceeds
- This results in the evaporation of as much as 50% of the liquid hydrogen over about 10 days
- Long-term storage of hydrogen requires that the hydrogen be converted from its Ortho form to its Para form to minimize boil-off losses
- This can be accomplished using a number of catalysts including activated carbon, platinized asbestos, ferric oxide, rare earth metals, uranium compounds, chromic oxide, and some nickel compounds

Ortho-para conversion--

A. Is a linear process in time
B. Obeys a power law in time
C. Is an exponential process in time
D. Is a logrithmic process in time
E. Obeys a dual power law in time

TS diagram for a pure substance

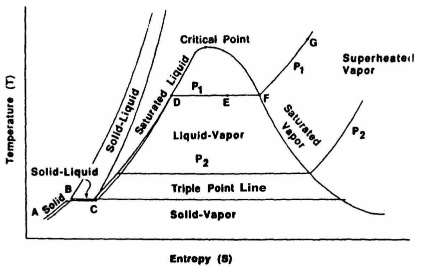


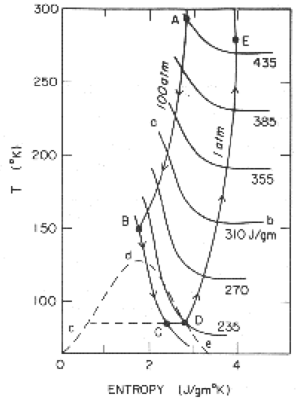
Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (2005), p. 82

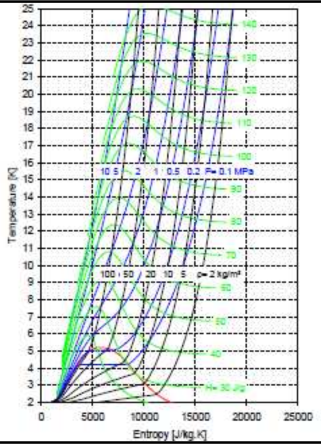
Liquefaction uses stages of compression with T constant and expansion with constant S. This diagram makes it easy to determine operating parameters and efficiencies. More complicated diagrams have lines of constant Enthalpy (H), which may be used when Joule-Thomson expansion produces cooling at very low T.

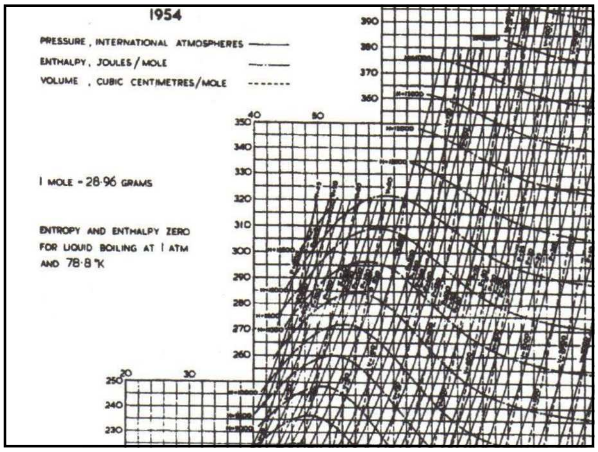
What is the Critical Point of a Fluid?

A. Point at which a gas liquefies
B. Point at which a liquid solidifies
C. Point where solid, liquid, and gas phases coexist
D. Point above which gas and liquid can not be distinguished
E. Point of no return

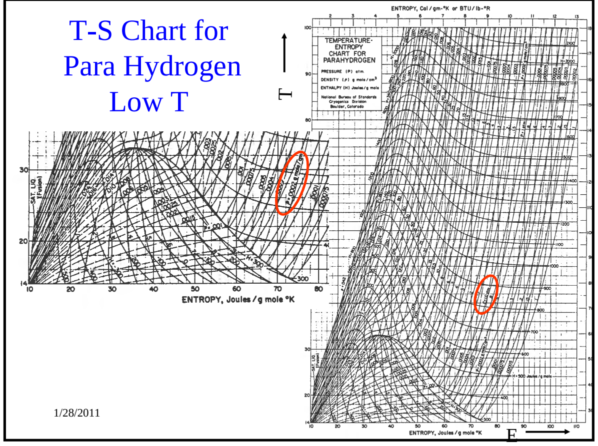
A Thermodynamic Cycle



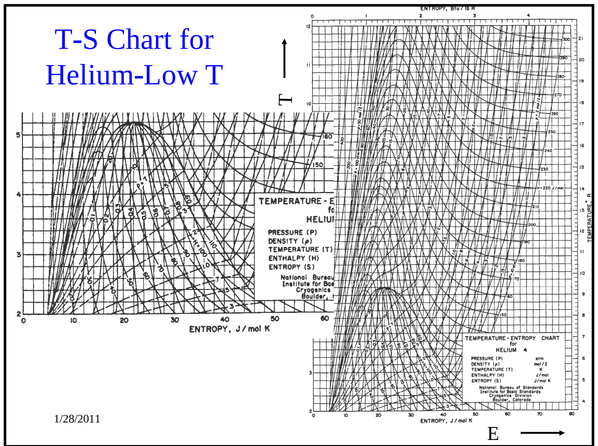




T-S Chart for Para Hydrogen Low T



T-S Chart for Helium-Low T



Milestones in hydrogen liquefaction

Date	Event
1898	Hydrogen first liquefied by James Dewar.
1898–mid 40s	Laboratory curiosity.
Mid 1940s–1956	Laboratory and pilot-scale liquefiers built to support U.S. nuclear weapons and aerospace programs. Largest unit: 0.45 ton/day at National Bureau of Standards.
1956–1959	U.S. Air Force and Air Products—“Bear” program:
1957	Baby Bear—Painsville, OH (0.75 ton/day)
1957	Mama Bear—West Palm Beach, FL (3.5 tons/day)
1959	Papa Bear—West Palm Beach, FL (30 tons/day)
1960–present	Several large-scale plants constructed in North America through private funding and operation. Examples:
1964	Linde 60 tons/day LH_2 plant in Sacramento, CA; largest ever built.
1965, 1976	Air Products builds two-plant, 66 tons/day LH_2 complex in New Orleans, LA.
1982–1990	Three LH_2 plants built in Canada—Air Products, Liquid Air, Airco.
1980s–present	LH_2 plants built in Europe and Japan.

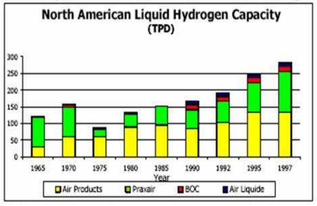
[a] All plant capacities given in U.S. tons/day.

Table adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 127

Liquid hydrogen production in the last 40 years

There are 10 hydrogen liquefaction plants in North America

- Train size ranges from 6 to 35 TPD (5,400 to 32,000 kg/day)



In the 1960's, liquid hydrogen plants were built to support the Apollo program. Today, liquid hydrogen is used to reduce the cost of hydrogen distribution.

- Delivering a full tube trailer of hydrogen to a customer results in a delivery of less than 300 kg
- A modern liquid hydrogen trailer carries 4000 kg of liquid hydrogen

Page adapted from Air Products

Hydrogen liquefaction plants in North America

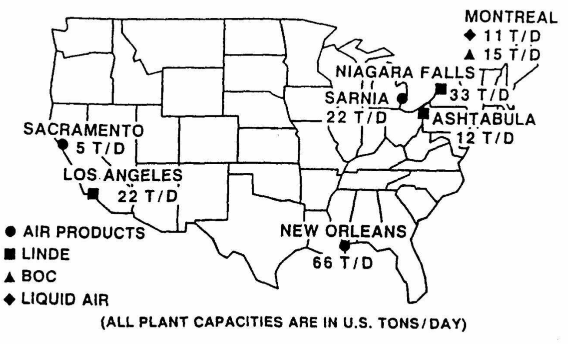
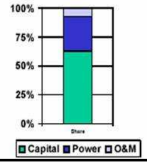


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 127

Economics of liquefaction

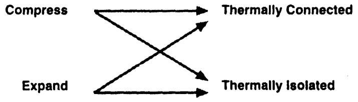
- **The plants are very capital intensive**
  - Praxair has started capacity expansions approximately once every 5 years since 1980. The infrequent builds means it's very difficult to reproduce designs.
  - While larger plants are more capital efficient, it's hard to take the capital risk of building the plant too large.
- **The process is very energy intensive**
  - Typical unit powers are on the order of 12.5 to 15 kWh_e/kg
- **The cost stack looks like:**



Page adapted from Air Products

"Four things that can be done to a gas"

according to Willie Gully (my former post doc)



Compress

Expand

Thermally Connected

Thermally Isolated

- **Compressing thermally connected to a reservoir**
  - Rejects heat to the reservoir at constant temperature
- **Compressing thermally isolated**
  - Causes the gas to heat
- **Expanding thermally connected to a reservoir**
  - Absorbs heat from the reservoir at constant temperature
- **Expanding thermally isolated**
  - Causes the gas to cool

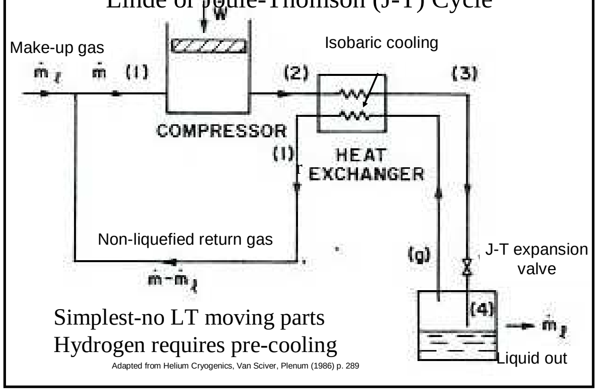
Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 274

Liquefaction Process

- The simplest liquefaction process is the Linde or Joule-Thompson expansion cycle
- Some of the steps in the process are
  - Gas is compressed at ambient pressure
  - Cooled in a heat exchanger
  - Passed through a throttle valve - isenthalpic Joule-Thompson expansion – producing some liquid
  - Liquid is removed and the cool gas is returned to the compressor via the heat exchanger of step #2

Liquefier block diagram

Linde or Joule-Thompson (J-T) Cycle

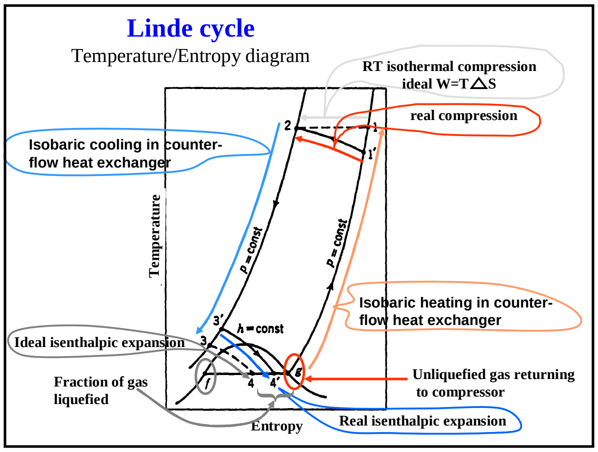


Simplest-no LT moving parts
Hydrogen requires pre-cooling

Adapted from Helium Cryogenics, Van Sciver, Plenum (1986) p. 289

Linde cycle

Temperature/Entropy diagram



Hydrogen requires more…

- The Linde cycle works for gases, such as nitrogen, that cool upon expansion at room temperature.
- But Hydrogen warms upon expansion at room temperature
- In order for hydrogen gas to cool upon expansion, its temperature must be below its pressure dependent inversion temperature $T_{J\text{-}T}$, where internal interactions allow the gas to do work when it is expanded. See graph on next slide.
- To reach the inversion temperature pre-cooling of the hydrogen gas to 78 K (-319°F) is done before the first expansion valve using LN2.
- The nitrogen gas may be recovered and recycled in a continuous refrigeration loop

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Inversion curve for various gases

Joule-Thomson Coefficient

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H$$

Note: The maximum T to begin hydrogen liquefaction is 202 K at 0 atm.

Since expansion must begin at a higher pressure, it is usually started below 100 K.

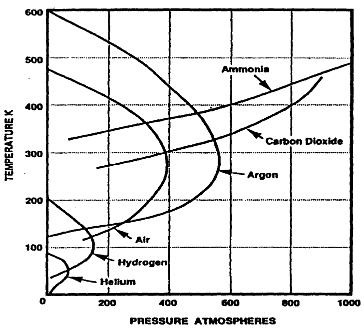


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 284

$$PV = nRT \qquad \mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H$$

Joule Thomson Coefficient for an Ideal Gas = ?

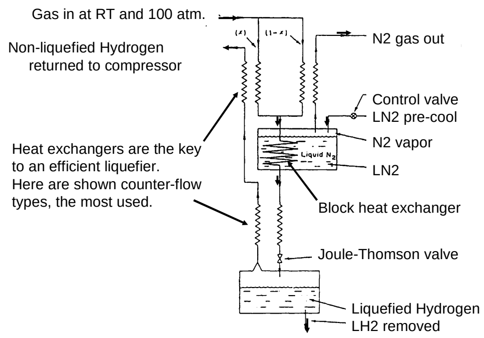
A. 0

B. V / nR

C. V

D. Can not be determined

Linde Cycle with pre-cooling



Gas in at RT and 100 atm.

Non-liquefied Hydrogen returned to compressor

N2 gas out

Control valve LN2 pre-cool

N2 vapor

LN2

Heat exchangers are the key to an efficient liquefier. Here are shown counter-flow types, the most used.

Block heat exchanger

Joule-Thomson valve

Liquefied Hydrogen LH2 removed

Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 304

Claude Cycle-How a Helium Liquefier Works

- Instead of pre-cooled Linde process—

Pass some high-pressure gas through an expansion engine, which then is sent to a heat exchanger to pre-cool the remaining g

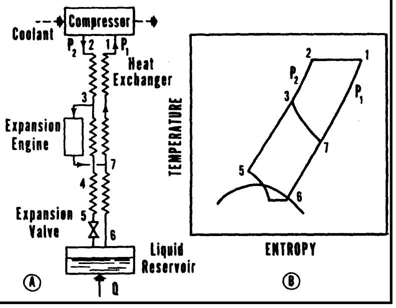
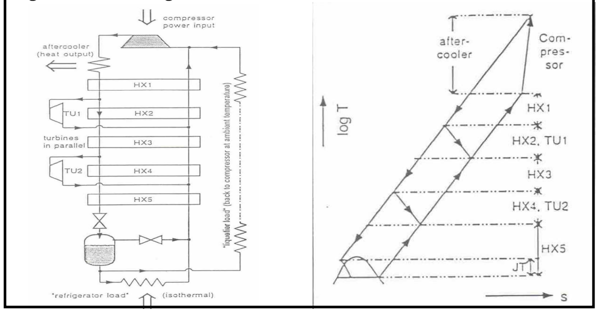


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 311

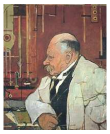
Claude Cycle: non-ideal isentropic plus isenthalpic expansion

In practice, an expansion engine can be used only to cool the gas stream, not to condense it because excessive liquid formation in the expansion engine would damage the turbine blades



First Liquefaction of Helium

Onnes use Claude cycle to liquefy helium in 1908, discover superconductivity in 1911


Heika Kamerlingh Onnes (1853-1926)

1913 Nobel physics prize "for his investigations..which led to the production of liquid helium"

Linde Cryogenics L1610 helium liquefier — UF 1993-present

Sam Collins-type machine using modified Claude cycle with two gas piston expanders

(similar to Koch 1410 liquefier—UF 1970-1980)

20 liters LHe per hour without LN_2 precooling

49 liters LHe per hour with LN_2 precooling

Flow diagram of KOCH 1410 helium liquefier (University of Florida 1970-1980)

Claude cycle/LN_2 pre-cool: 2 expansion engines/heat exchangers and JT valve

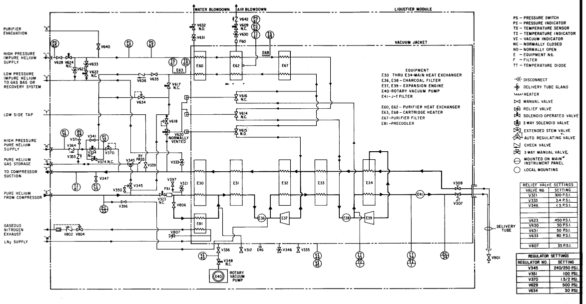


FIGURE 4-1 FLOW DIAGRAM MODEL 1410 HELIUM LIQUEFIER

In the Claude refrigeration cycle--

A. Pressure drop across the JT-valve is reduced in order to increase $\Delta T = T_{RT}-T_{JT}$

B. Gas flow rate to JT-valve is sacrificed in order to increase ΔT

C. Both A and B are true

D. Neither A nor B are true

Ideal Liquefaction and other cycles

- Ideal work of liquefaction for hydrogen is3.228 kWh/kg (1.464 kWh/lb).
- Ideal work of liquefaction for helium-4 is 1.91 kWh/kg (0.87 kWh/lb)
- Ideal work of liquefaction for nitrogen is 0.207 kWh/kg (0.094 kWh/lb)

Other processes for liquefaction include

Dual-Pressure Linde Process
Dual-Pressure Claude Cycle
Haylandt Cycle

These are similar to the processes described above, but use extra heat exchangers, multiple compressors, and expansion engines to reduce the energy required for liquefaction (increasing the capital cost).

Areas of possible improvement

- **More cost effective LH2 production systems**
  - System modularization for traditional sized units
  - Larger scale equipment
  - Higher efficiency compressors and expanders
  - More efficient refrigeration
  - Lower cost high-efficiency insulation
- **Cost effective small scale hydrogen generation**
  - Low cost high pressure compressors and expanders
  - Novel low-temperature refrigeration
  - Low heat leak liquid storage units

Adapted from Praxair

Compressing hydrogen

- **Hydrogen is difficult to compress**
  - Very small molecule
  - Positive displacement compressors are used
- **Hydrogen compressors are expensive**
  - Materials
  - Size
  - Redundancy required for reliability
- **The process is energy intensive**
  - Typical unit powers are:

Inlet-Outlet(psig)	Adiabatic Efficiency	Compression Energy
300 - 1,000	70-80%	0.6 - 0.7 kWh_e/kg
100 - 7,000	50-70%	2.6 - 3.6 kWh_e/kg

Adapted from Praxair

Assignments for next 3 classes

Jan. 13 (Thursday): Grad students meet outside Helium Liquefier Room
B125 NPB (undergrads welcome but not required)
After tour go to the CryoNet page and explore:
http://www.phys.ufl.edu/~cryogenics/cryonetd.htm
http://www.phys.ufl.edu/~cryogenics/cryonetd.htm

Graduate Students: write 500 word report on what you learned on the tour and submit by email (subject: lab tour 1) to me by Jan. 20.

Jan. 18 & 20 (next week): No classes-watch the movie **Absolute Zero** on
your computer
http://www.youtube.com/watch?v=y2jSv8PDDwA

http://www.youtube.com/watch?v=y2jSv8PDDwA

Do the following interactive exercises on the Nova website
http://www.pbs.org/wgbh/nova/zero/

http://www.pbs.org/wgbh/nova/zero/

1. *A sense of scale*; 2. *Milestones*; 3. *How low can you go* - report the series of gases you use and your lowest temperature to me; 4. *States of matter* - report what temperatures and pressures you found bracketed the liquid/gas transition for hydrogen; 5. *Anatomy of a refrigerator*