Liquefaction of “Permanent” Gases

Hydrogen as an example

See Flynn Ch. 3 and 6

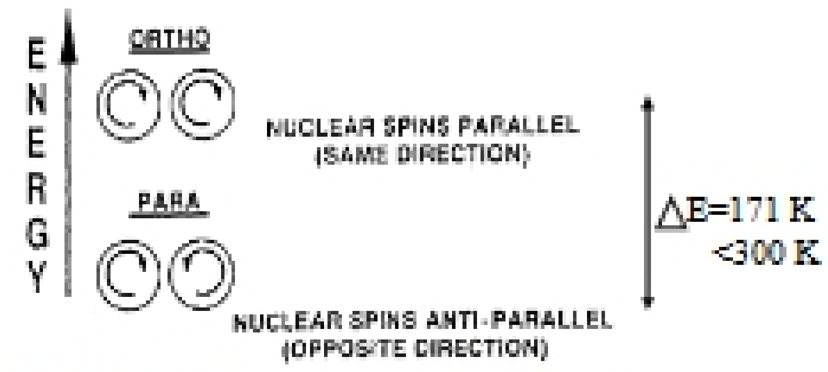
Liquefaction of Hydrogen

- 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

Two forms of hydrogen molecule



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→p = 0.15 kWh/kg } more energy to convert than liquefy
Heat of liquefaction = 0.12 kWh/kg

Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker-NY (1997), p. 138

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

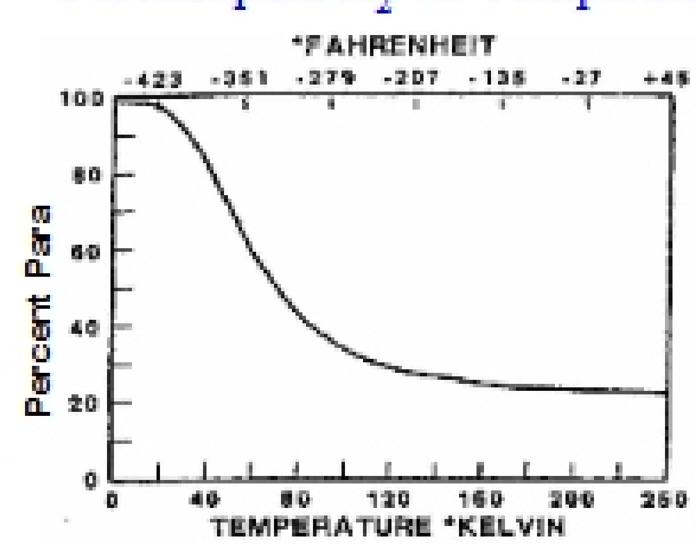
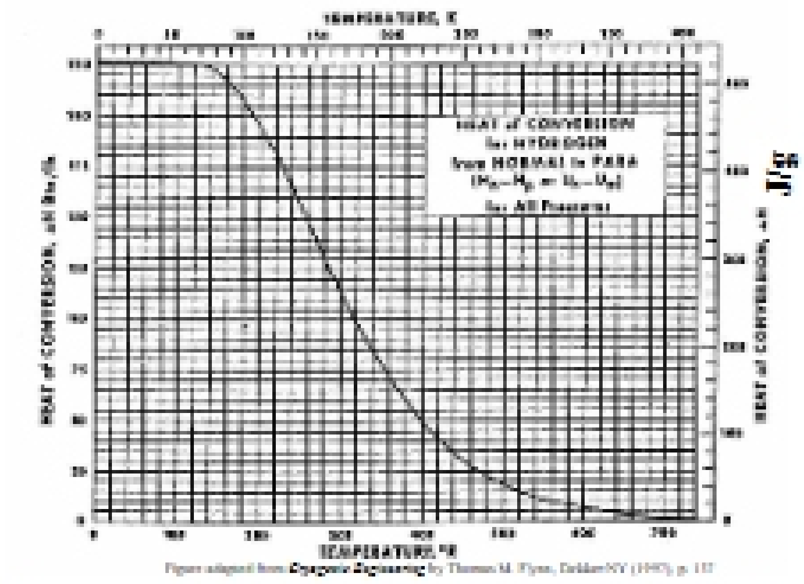


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker-NY (1997), p. 139

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

Heat of Normal-to-Para conversion



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

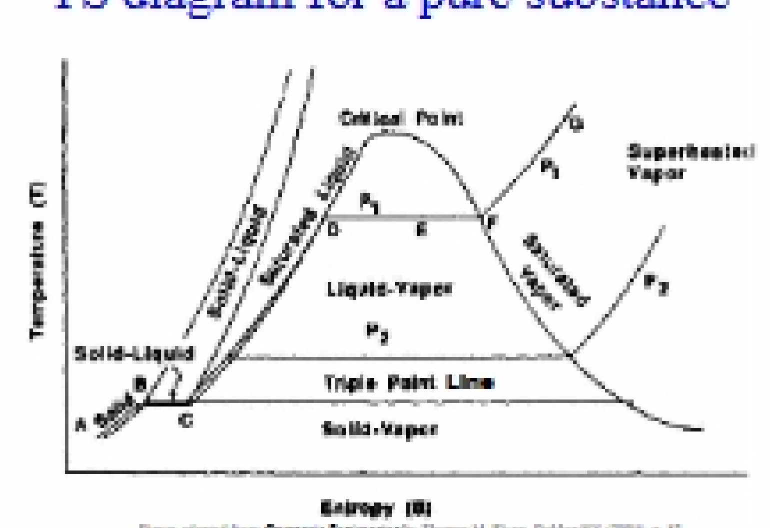
Ortho-Para conversion notes

- 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

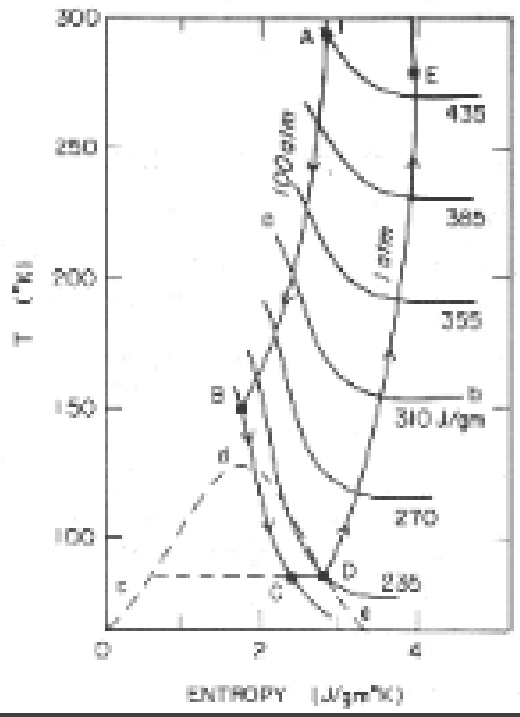


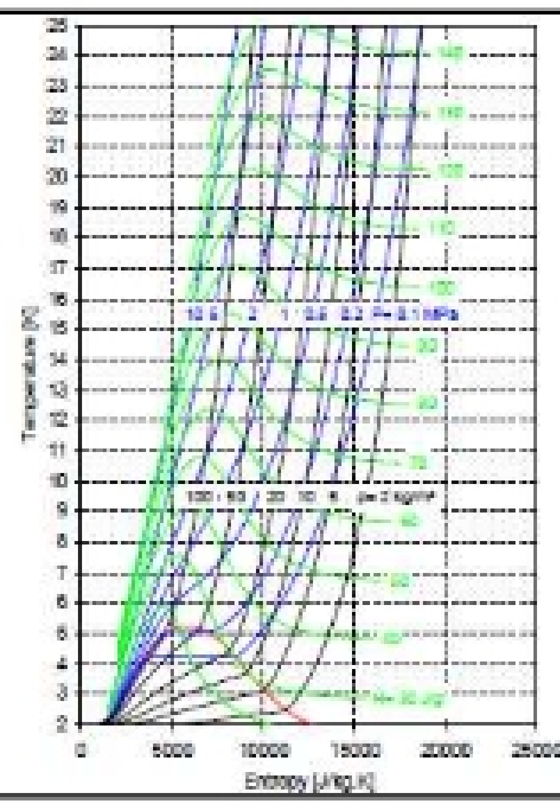
Liquefaction uses stages of compression with T constant and expansion with constant S. This diagram makes it easy to determine operating parameters and efficiencies. More complicated diagrams have lines of constant Enthalpy (H), which may be used when Joule-Thomson expansion produces cooling at very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

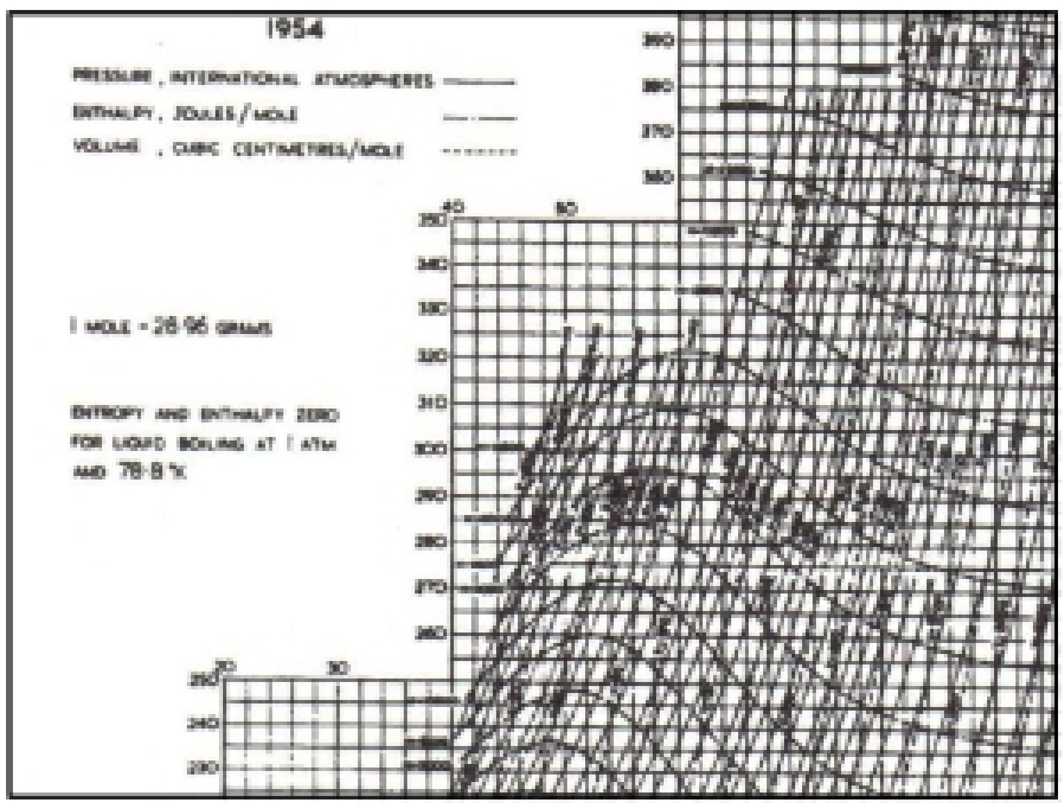
What is the Critical Point of a Fluid?

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

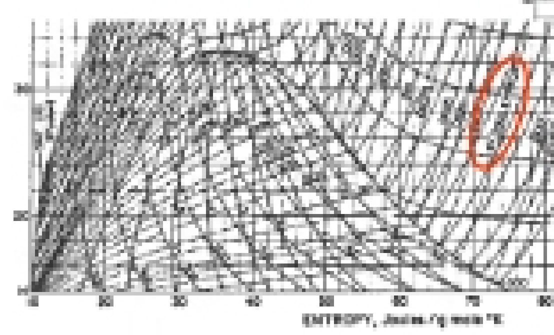
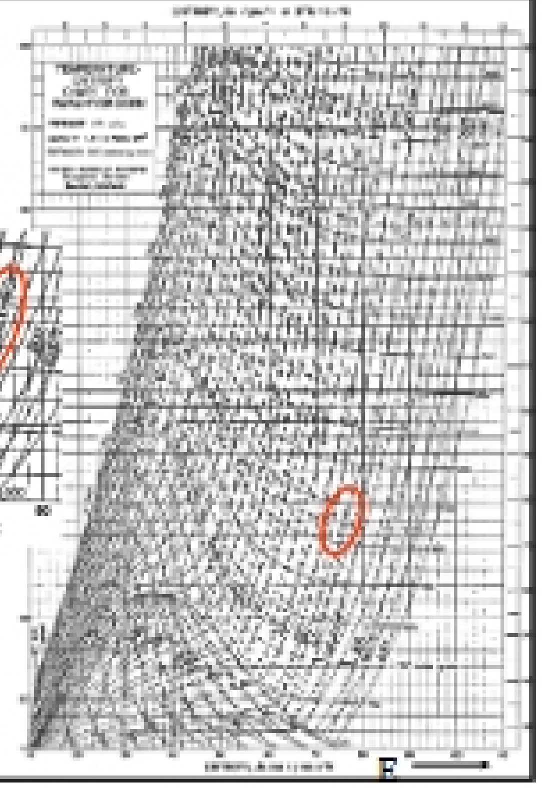
A Thermodynamic Cycle



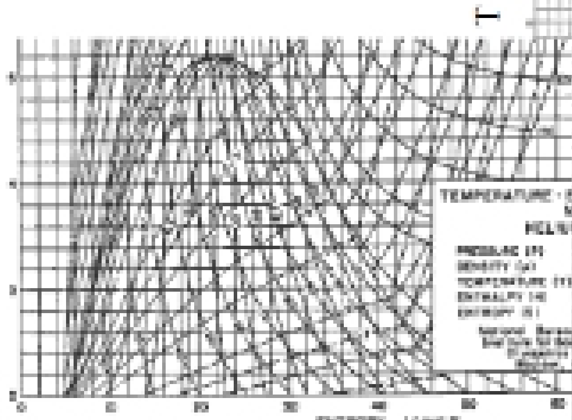
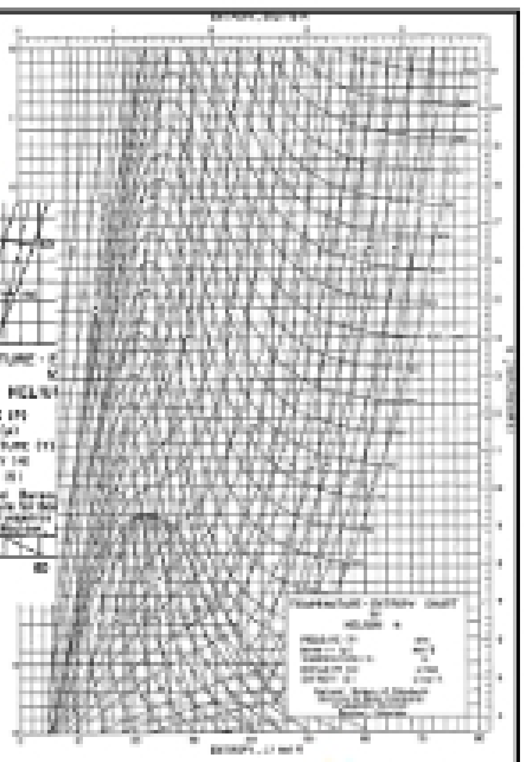




T-S Chart for Para Hydrogen Low T

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—Painesville, 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.

*All plant capacities given in U.S. tons/day.

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