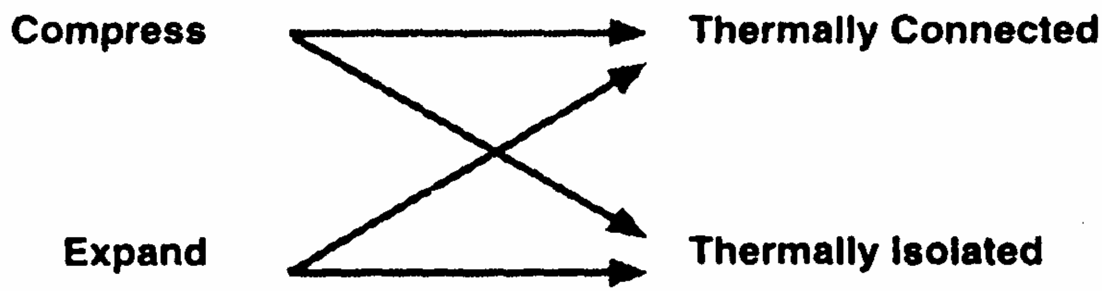
LECTURE # 11

Topic:

Liquefaction

"Four things that can be done to a gas"

according to Willie Gully



- 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

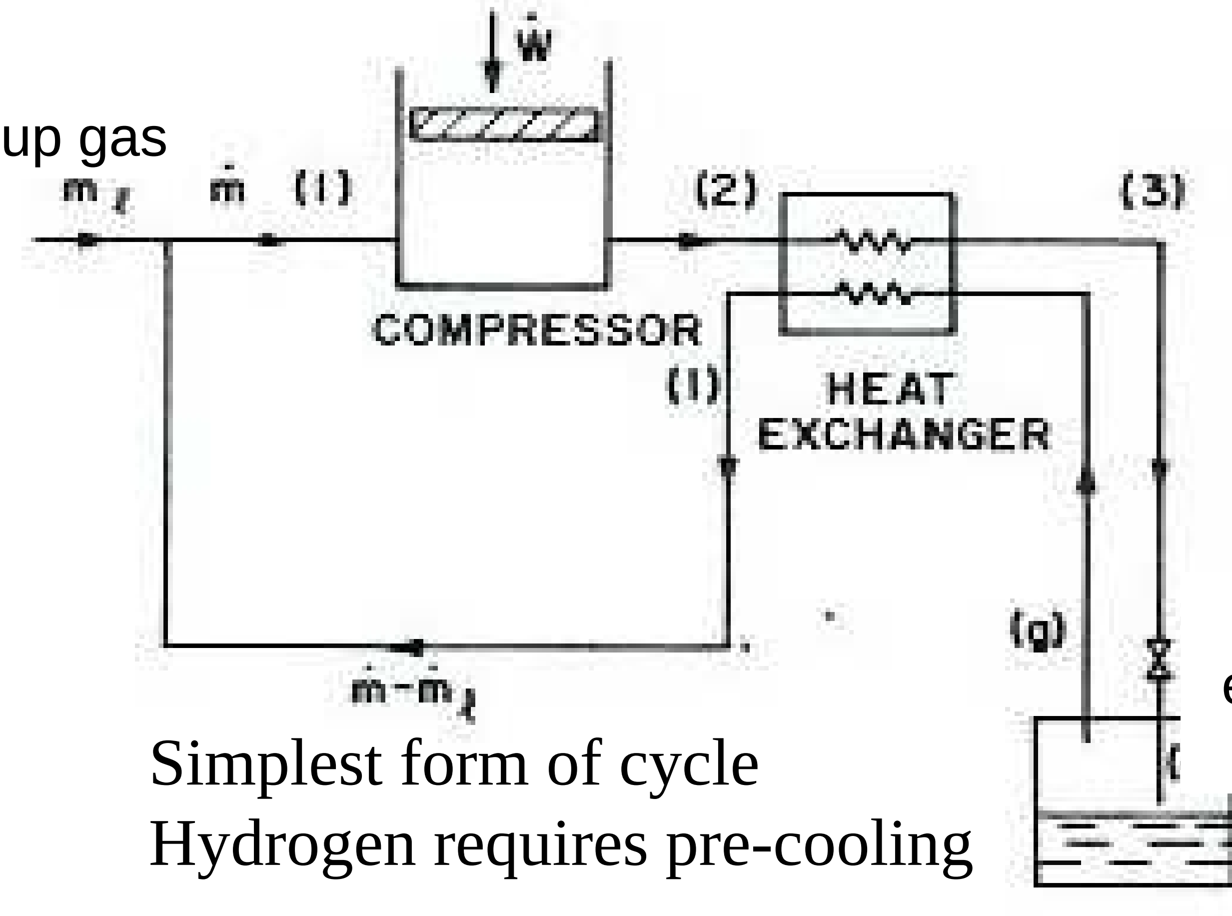
Liquefaction Process

- 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-Thomson (J-T) Cycle

Make-up gas



J-T expansion valve

Liquid out

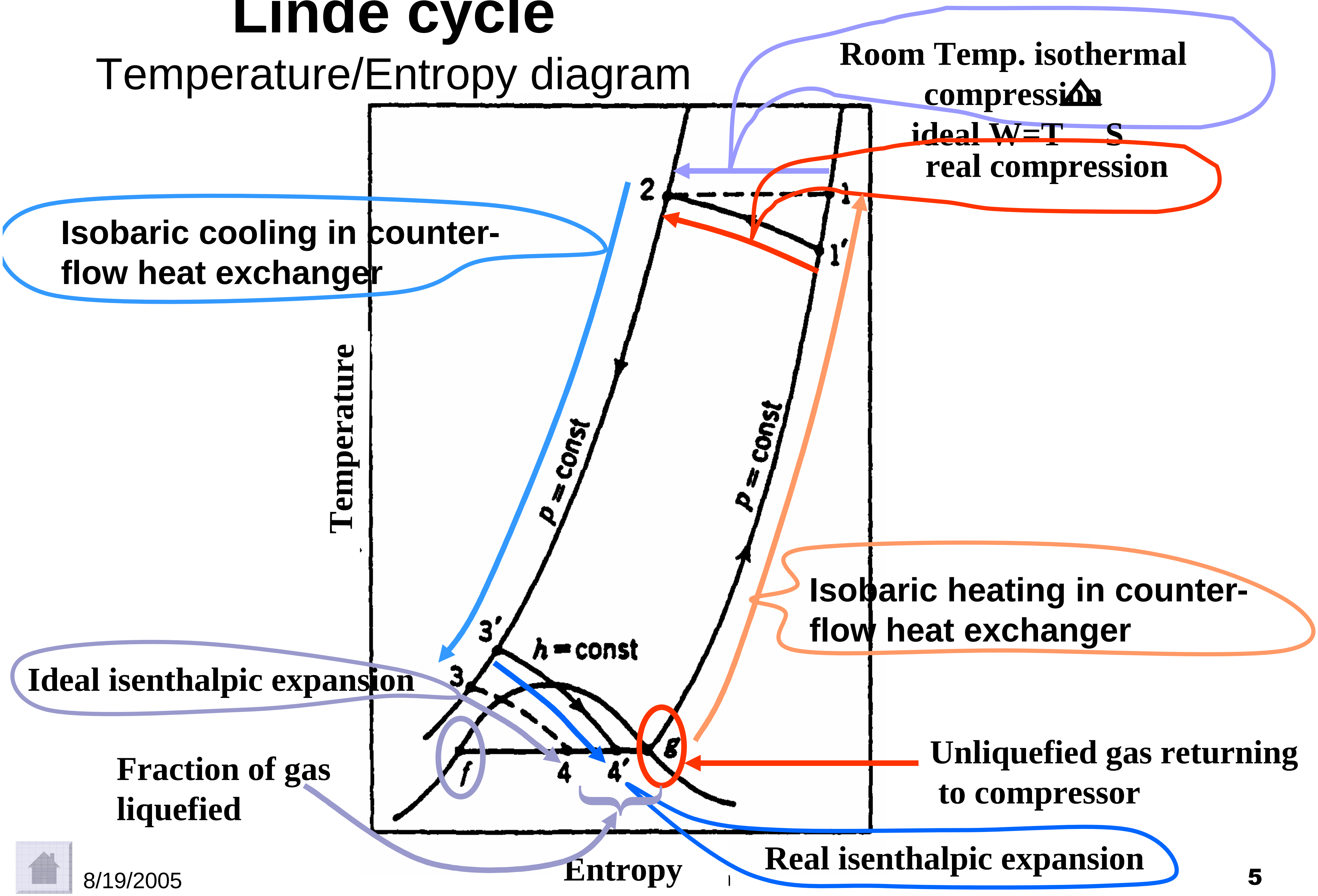
Simplest form of cycle

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 liquid nitrogen.
- The nitrogen gas may be recovered and recycled in a continuous refrigeration loop

Inversion curve for various gases

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.

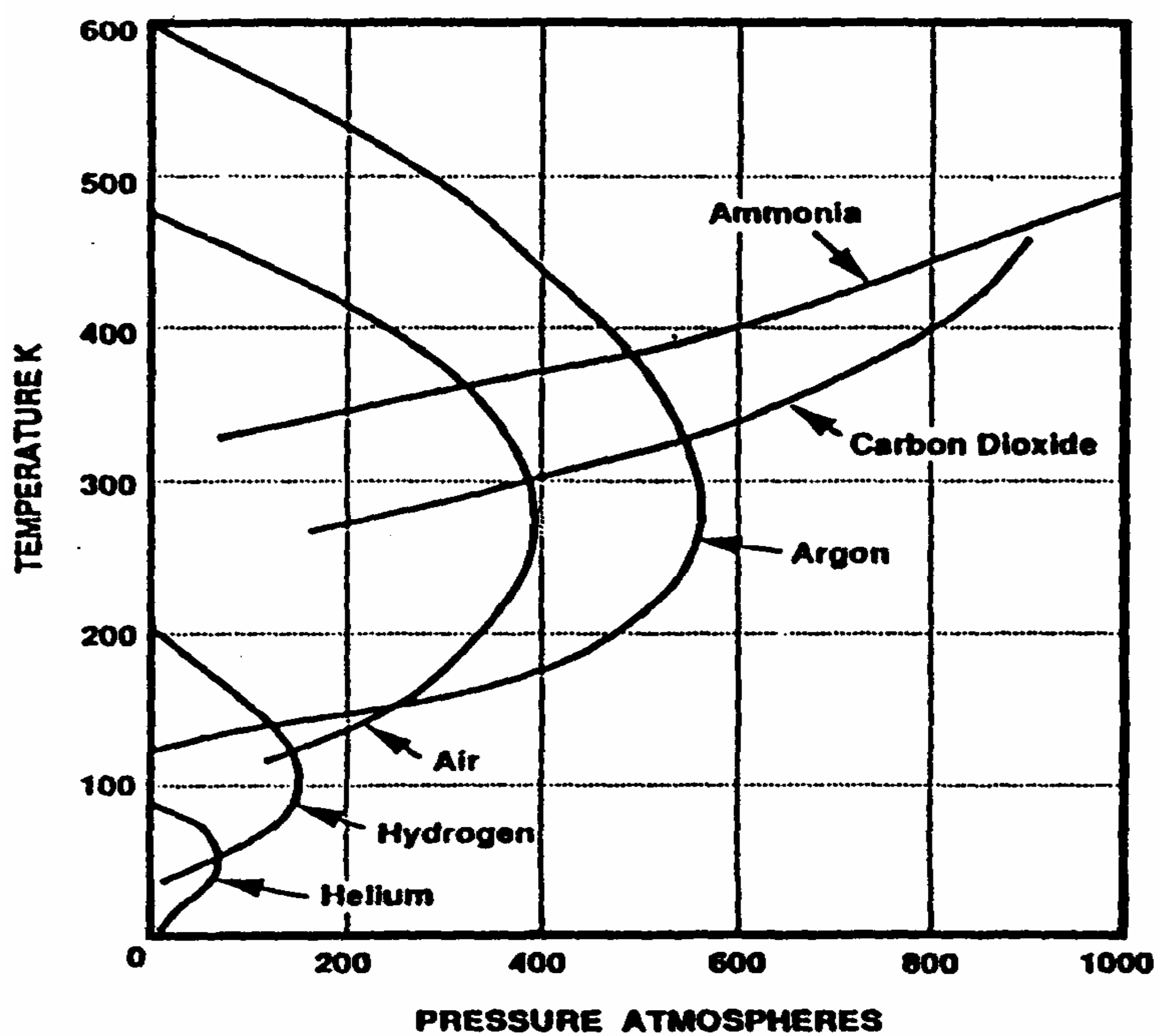


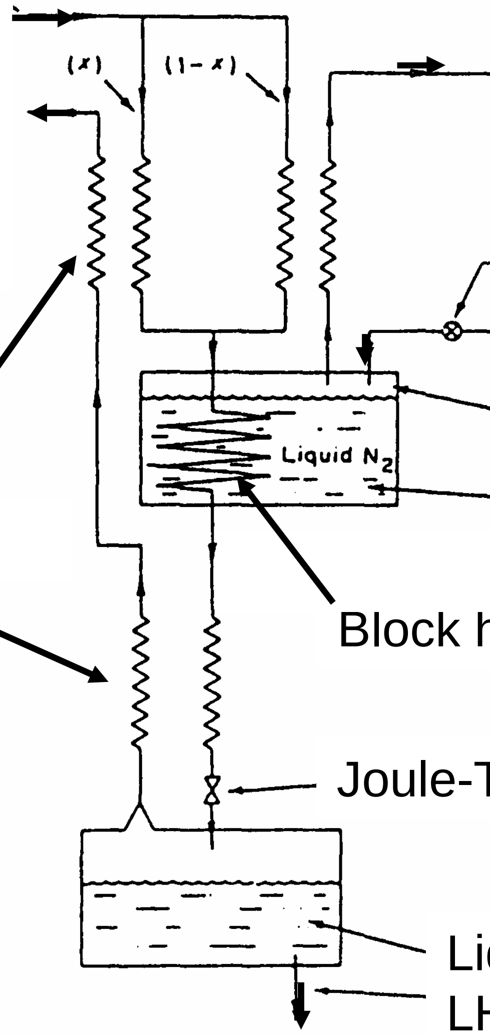
Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 284

Linde Cycle with pre-cooling

Gas in at room temp and 100 atm.

Non-liquefied Hydrogen returned to compressor

Heat exchangers are the key to an efficient liquefier. Here are shown counter-flow types. These are common in this application.



N2 gas out

Control valve LN2 pre-cool

N2 vapor

LN2

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

- An alternative to the pre-cooled Linde process is to pass some of the high-pressure gas through an expansion engine, which then is sent to a heat exchanger to cool the remaining gas.
- Theoretical process referred to as *ideal liquefaction* uses a reversible expansion process to reduce the energy required for liquefaction.
- It consists of an isothermal compressor
- Followed by an isenthalpic expansion to cool the gas and produce a liquid
- 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

Claude Cycle: non-ideal isentropic plus isenthalpic expansion

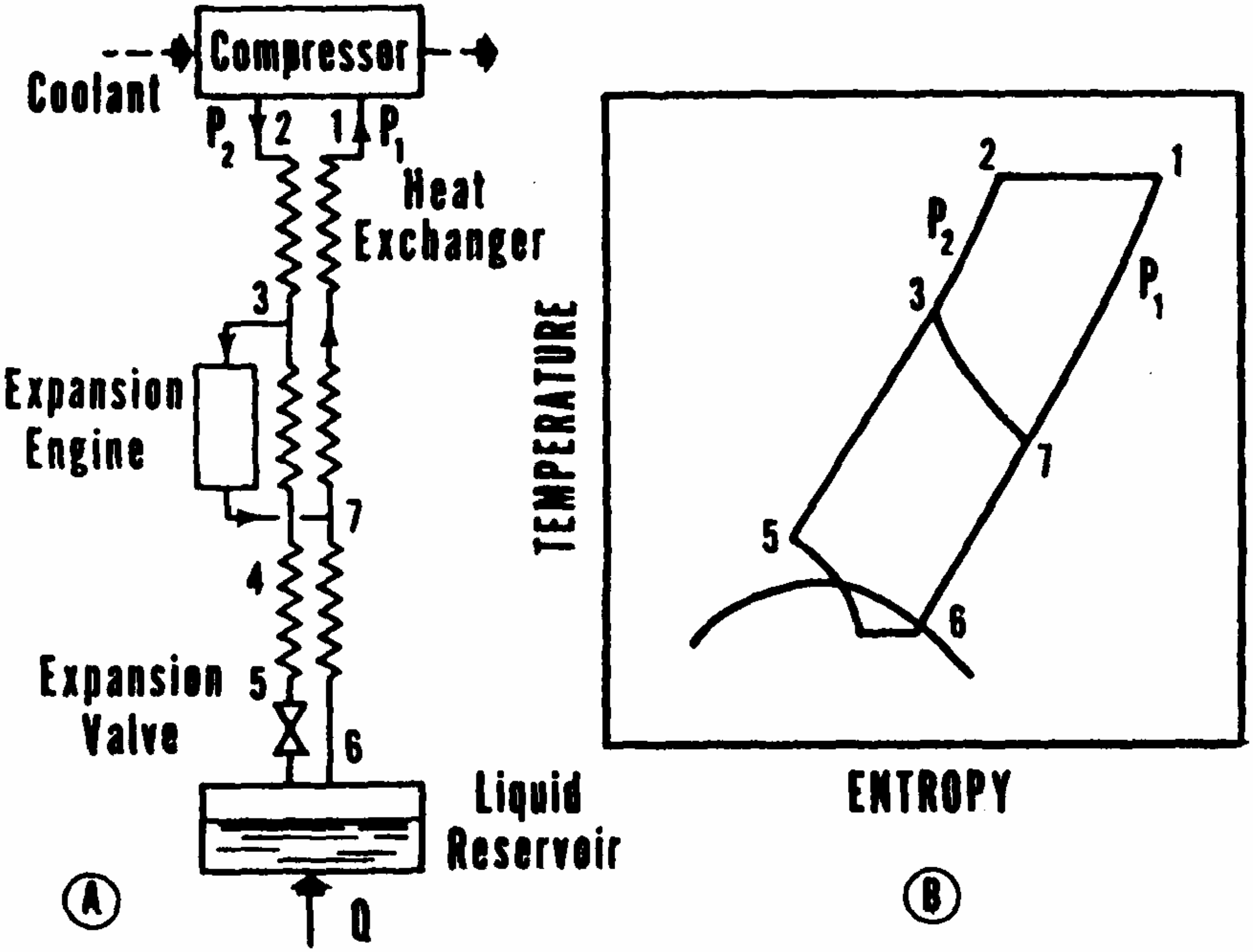


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 311

Ideal Liquefaction and other cycles

- The ideal work of liquefaction for hydrogen is 3.228 kWh/kg (1.464 kWh/lb).
- The ideal work of liquefaction for nitrogen is only 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)

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])

Ortho-Para conversion

- 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 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

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