

Refrigeration & Liquefaction

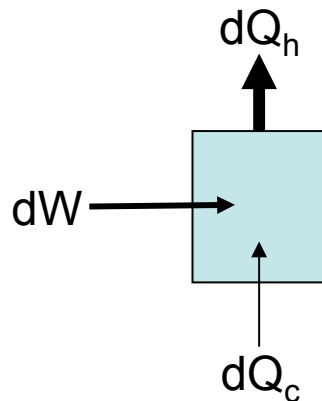


Outline

- Recuperative systems
 - Ideal refrigeration / liquefaction
 - Joule Thomson expansion
 - System analyses: 1st and 2nd law applied to:
 - Simple Linde-Hampson cycle
 - Variations and improved performance cycles
 - Claude and Collins cycles

Ideal Refrigeration/Liquefaction

- ‘Moving’ heat from a cold reservoir to a warm reservoir requires energy



The amount of heat moved is associated with an amount of entropy by the relationship:

$$dQ = TdS$$

- In an ideal process, the entropy associated with the two heat flows is the same, that is:

$$dS = \frac{dQ_c}{T_c} = \frac{dQ_h}{T_h}$$

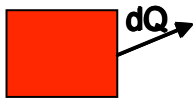
- In an ideal process the amount of work (energy) required to ‘move’ the heat is

$$dW = dQ_h - dQ_c$$

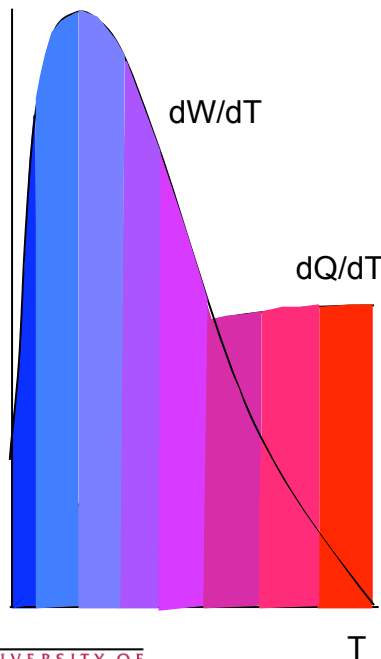


Ideal Cool Down

- Extracting an amount of heat to lower the temperature of (whatever) by dT , and releasing the heat at T_h :



$$dQ = mc_p dT, \quad dW = dQ_h - dQ = mc_p \left(\frac{T_h}{T} - 1 \right) dT$$



Including the temperature dependence of the specific heat, the ideal cool down work becomes:

$$\Delta W = \int_{T_c}^{T_h} mc_p(T) \left[\frac{T_h}{T} - 1 \right] dT$$

Compare this to the amount of energy required to warm up the same mass:

$$\Delta E = \int_{T_c}^{T_h} mc_p(T) dT$$



Ideal Liquefaction

- To cool down a parcel of gas, and convert it from saturated vapor to saturated liquid at its normal boiling temperature:

Temperature dependent specific heat

$$\Delta W = \underbrace{\int_{T_{nbp}}^{T_h} mc_p(T) \left[\frac{T_h}{T} - 1 \right] dT}_{\text{Work to extract sensible heat}} + \underbrace{mh_{fg} \left[\frac{T_h}{T_{nbp}} - 1 \right]}_{\text{Work to extract latent heat}}$$

Work to extract sensible heat Work to extract latent heat

- Re-arranging terms we have:

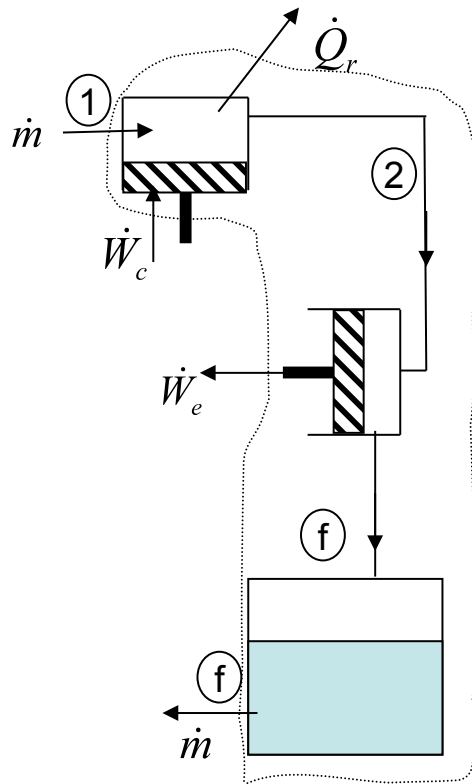
$$\Delta W = mT_h \left[\int \frac{c_p(T)}{T} dT + \frac{h_{fg}}{T_{nbp}} \right] - m \left[\int c_p dT + h_{fg} \right]$$

$$\Delta W = mT_h \Delta s - m \Delta h$$

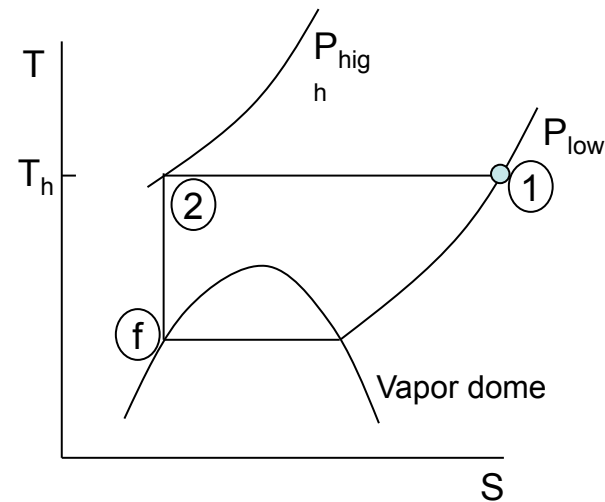
- Or, in the 'rate' form:

$$\dot{W} = \dot{m}T_h \Delta s - \dot{m} \Delta h$$

Ideal Liquefaction



A 1st-law, 2nd-law analysis around an ideal cycle reveals the same expression



1st law: Energy balance around system:

In steady state, the sum of the energies into and out of the system = 0

$$\dot{W}_c + \dot{m}h_1 = \dot{W}_e + \dot{Q}_r + \dot{m}h_f \quad \text{or} \quad \dot{W}_{net} = \dot{Q}_r - \dot{m}(h_1 - h_f)$$

2nd law: Entropy balance around system:

In steady state, the sum of the entropies into and out of the system = 0

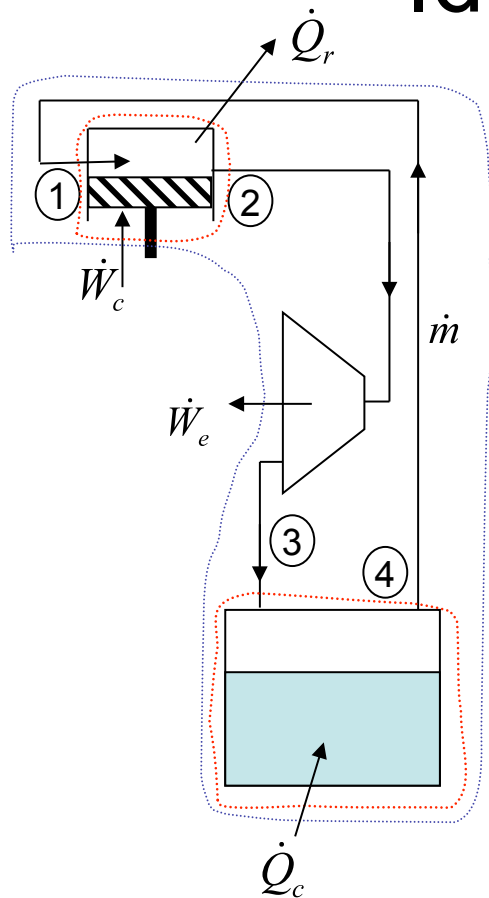
$$\dot{m}s_1 = \dot{m}s_f + \frac{\dot{Q}_r}{T_1} + \dot{\phi}^0 \quad \text{or} \quad \dot{Q}_r = T_1\dot{m}(s_1 - s_f)$$

Combining, we have:

$$\dot{W}_{net} = T_1\dot{m}(s_1 - s_f) - \dot{m}(h_1 - h_f)$$

Note the SI units of h(kJ/kg) and s(kJ/kg-K)

Ideal Refrigeration



- In steady state, the 1st law around the whole system gives:

$$\dot{W}_c - \dot{W}_e = \dot{Q}_r - \dot{Q}_c \quad \text{or} \quad \dot{W}_{net} = \dot{Q}_r - \dot{Q}_c$$

- The 2nd law around the compressor gives:

$$\dot{Q}_r = T_H \dot{m} (s_1 - s_2)$$

- The 2nd law around the evaporator gives:

$$\dot{Q}_c = T_c \dot{m} (s_4 - s_3)$$

- Combining, and noting that $s_1 = s_4$ and $s_2 = s_3$ we have:

$$\frac{\dot{W}_{net}}{\dot{m}} = (T_H - T_c)(s_4 - s_3) = \frac{\Delta S}{\dot{m}} (T_H - T_c) = \frac{\dot{Q}_c}{\dot{m}} \left(\frac{T_H}{T_c} - 1 \right)$$

- The coefficient of performance (COP) for the refrigerator is then

$$COP_{ideal} \equiv \frac{\dot{Q}_c}{\dot{W}_{net}} = \left(\frac{T_H}{T_c} - 1 \right)^{-1} = \frac{T_c}{T_H - T_c}$$

Ideal Liquefaction / Refrigeration

Table 3.1. Ideal-work requirements for liquefaction of gases beginning at 300 K (80°F) and 101.3 kPa (14.7 psia)

Gas	Normal Boiling Point		Ideal Work of Liquefaction, $-\dot{W}_d/\dot{m}_f$	
	K	°R	kJ/kg	Btu/lb _m
Helium-3	3.19	5.74	8 178	3 516
Helium-4	4.21	7.58	6 819	2 931
Hydrogen, H ₂	20.27	36.5	12 019	5 167
Neon, Ne	27.09	48.8	1 335	574
Nitrogen, N ₂	77.36	139.2	768.1	330.2
Air	78.8	142	738.9	317.7
Carbon monoxide, CO	81.6	146.9	768.6	330.4
Argon, A	87.28	157.1	478.6	205.7
Oxygen, O ₂	90.18	162.3	635.6	273.3
Methane, CH ₄	111.7	201.1	1 091	469
Ethane, C ₂ H ₆	184.5	332.1	353.1	151.8
Propane, C ₃ H ₈	231.1	416.0	140.4	60.4
Ammonia, NH ₃	239.8	431.6	359.1	154.4

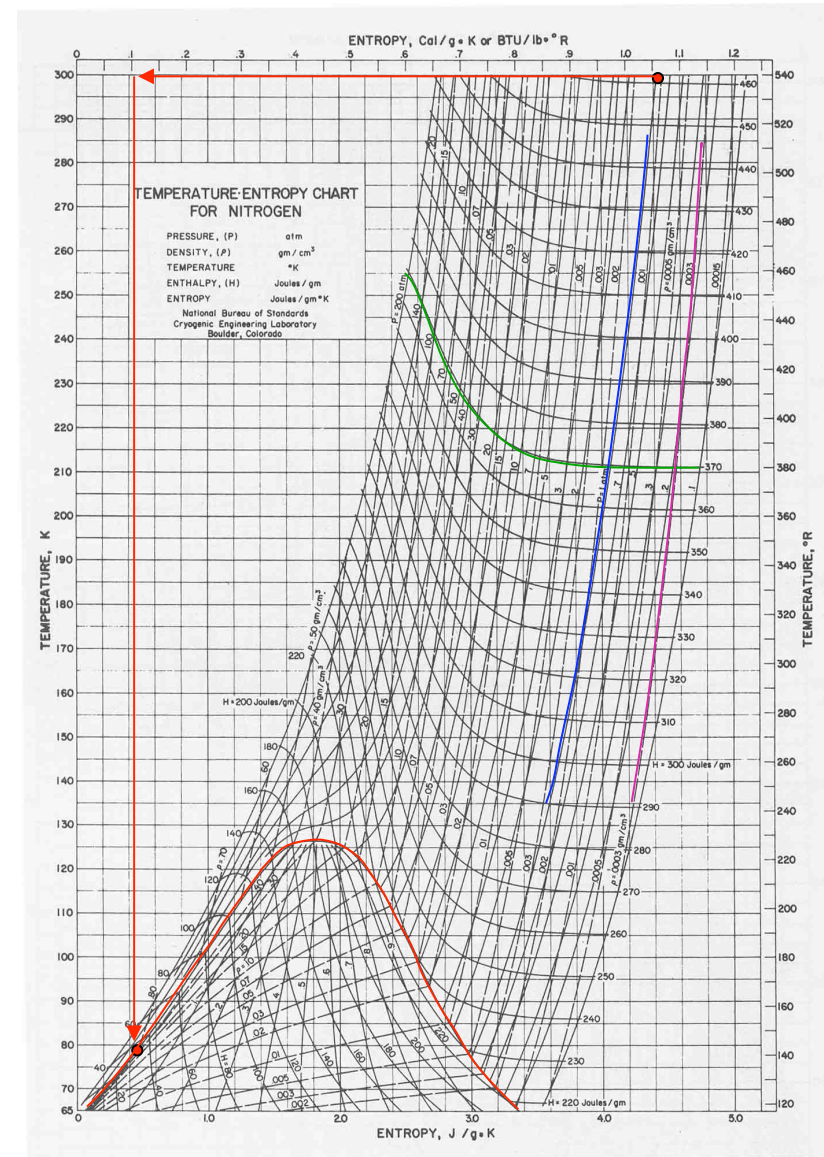
- Ideal liquefaction work for cryogenics (from Barron)
- Comparison with ideal performance defined by Figure of Merit (FOM), for refrigeration sometimes referred to as “% of Carnot.”

$$FOM_{liquefier} = \frac{\left(\frac{\dot{W}_{net}}{\dot{m}_f}\right)_{ideal}}{\left(\frac{\dot{W}_{net}}{\dot{m}_f}\right)_{actual}}$$

$$FOM_{refrigerator} = \frac{COP_{actual}}{COP_{ideal}}$$

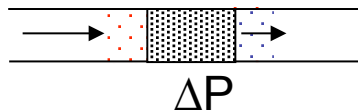
Practical Limitations

- Not possible to achieve ideal-scenario pressure
 - Inspect T-S diagram: find lines of constant **pressure**, constant **enthalpy**, constant **density**, **vapor dome**
 - Estimate required pressure for 'ideal' liquefaction of nitrogen
- Isentropic expansion is very difficult to achieve.
 - Isenthalpic (or throttle) expansion is very easy to achieve
 - Cooling associated with throttle process exploits 'real-gas' properties. Note that at high T, low P, h is independent of pressure, but elsewhere it is not.

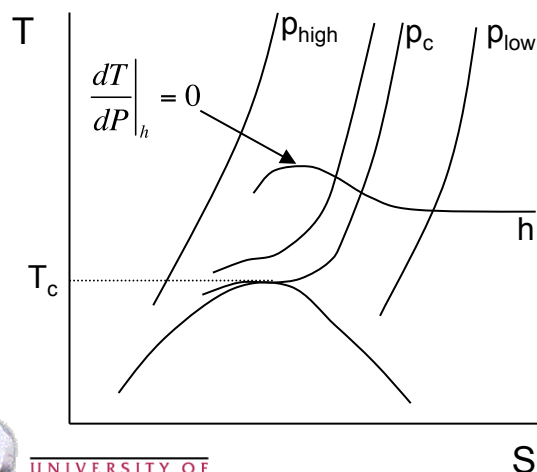


Joule-Thomson Coefficient

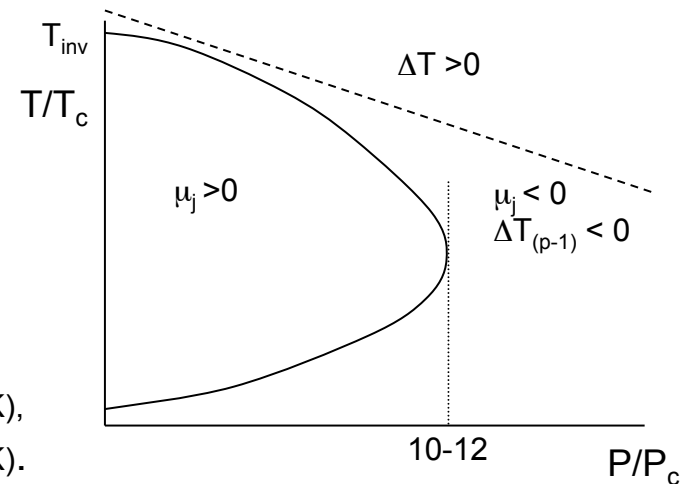
- 1885 - Joule & Thomson (Lord Kelvin) confirm that a gas flow through a restriction experiences a temperature drop along with the pressure drop.



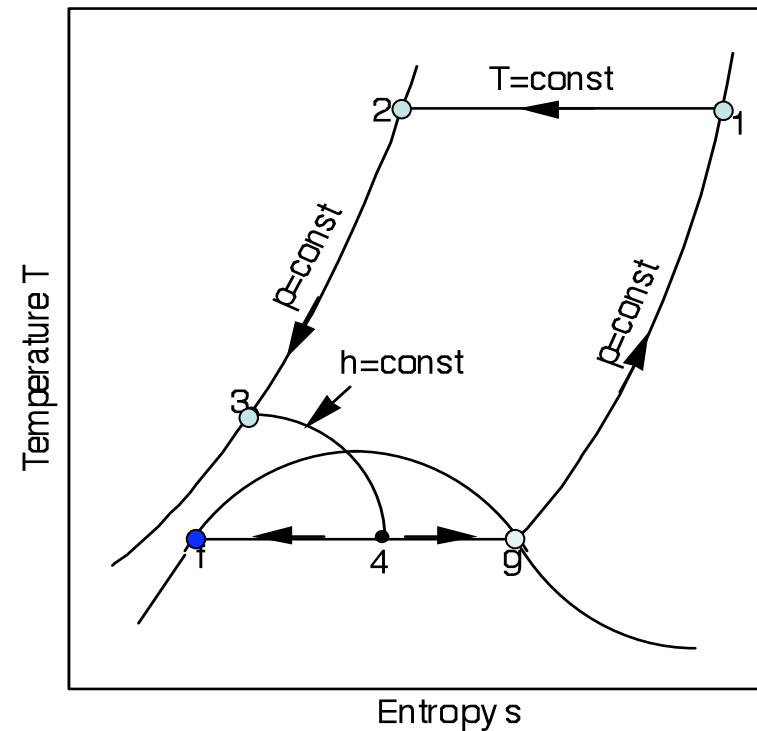
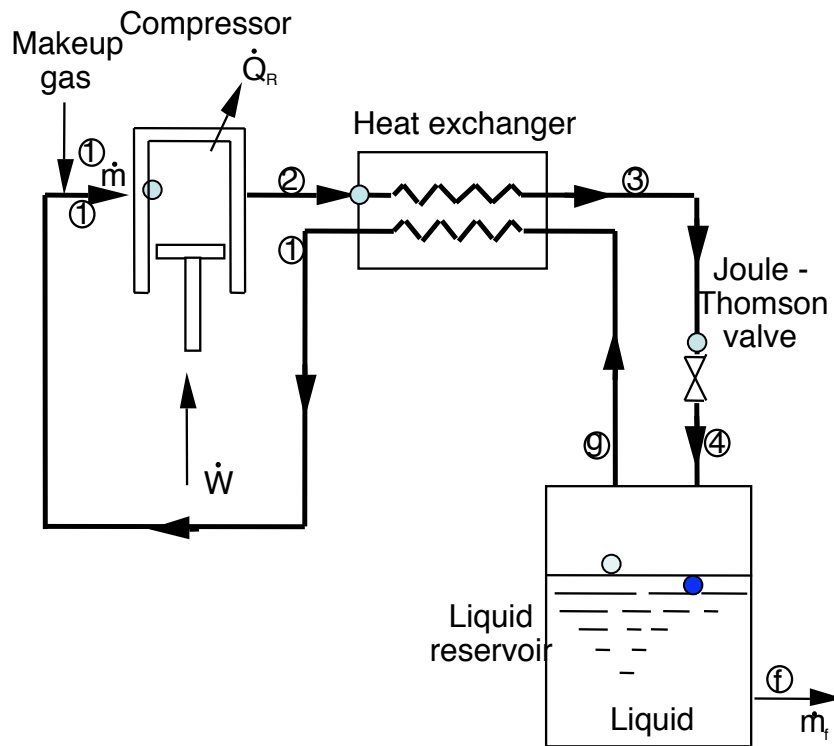
- The Joule-Thomson coefficient: $\mu_j = \left. \frac{dT}{dP} \right|_h$ characterizes the phenomenon.
- When $\mu_j > 0$, cooling accompanies a pressure drop.
- Regions of positive and negative μ_j are reflected in T-S diagrams and inversion curves:



- Above the inversion temperature, we have $\mu_j \leq 0$ for all pressures.
- Pre-cooling is required for helium ($T_{inv}=45K$), hydrogen ($T_{inv}=205K$), and neon ($T_{inv}=250K$).



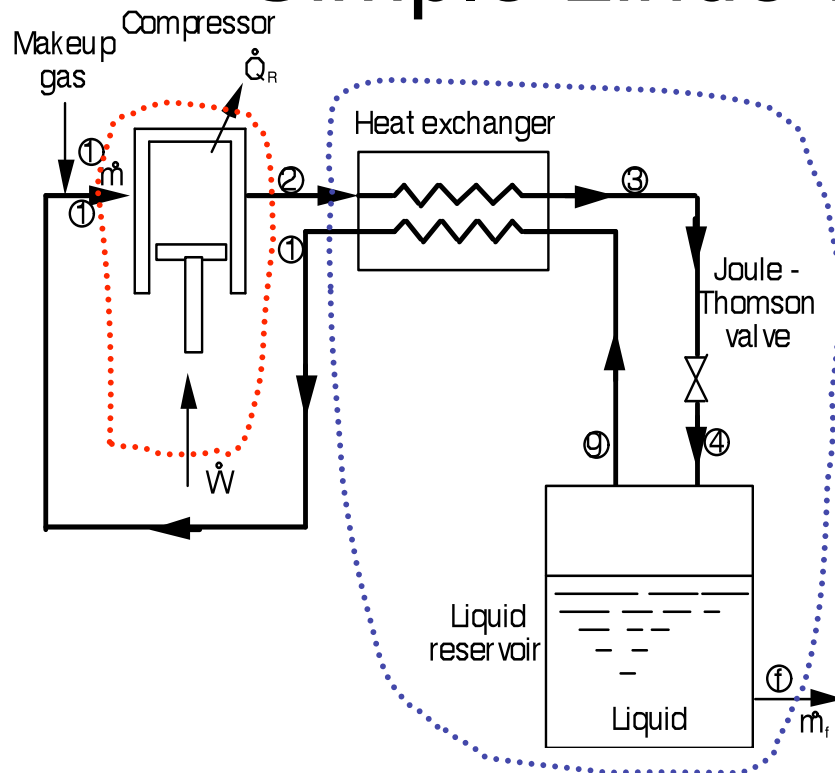
Simple Linde-Hampson Cycle



- Inversion temperature must be above compression temperature, or pre-cooling via a higher temperature refrigerant liquid is required.
- Recuperative heat exchanger pre-cools high pressure stream.
- Liquefier requires source of make-up gas.
- Refrigerator absorbs heat converting liquid to vapor at saturation temperature of low pressure.



Simple Linde-Hampson Cycle



- In steady state conditions, the 1st law around the compressor gives:

$$\dot{W}_c - \dot{Q}_r + \dot{m}(h_1 - h_2) = 0$$

- The 2nd law around the compressor gives:

$$\dot{m}s_1 = \dot{m}s_2 + \frac{\dot{Q}_r}{T_1} \quad \text{or} \quad \dot{Q}_r = \dot{m}T_1(s_1 - s_2)$$

(Note the assumption of isothermal compression)

- Combining, we have:

$$\frac{\dot{W}_c}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2)$$

- Applying the 1st law around everything except the compressor gives:

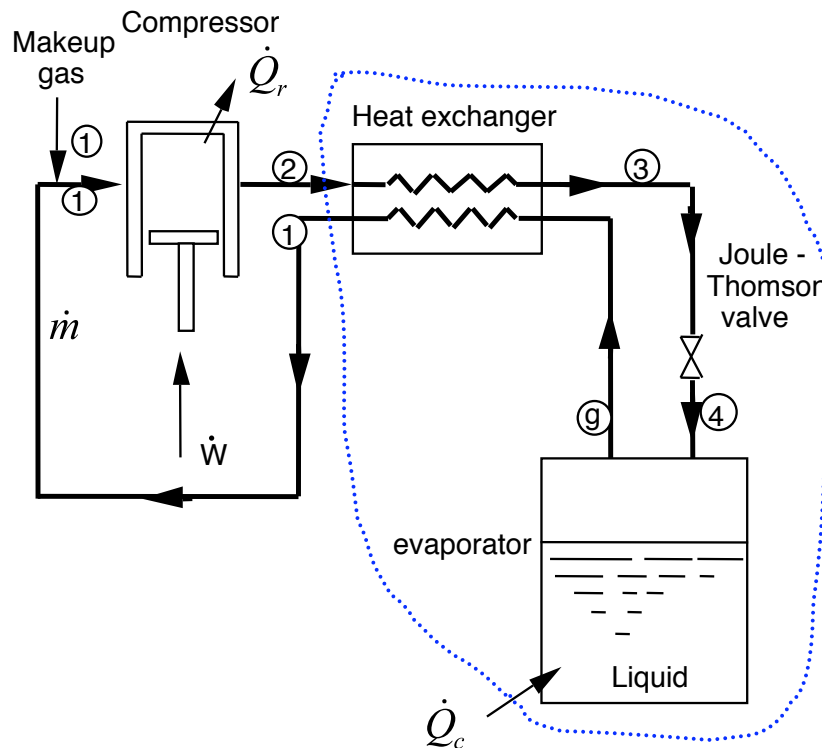
$$\dot{m}h_2 - (\dot{m} - \dot{m}_f)h_1 - \dot{m}_f h_f = 0 \quad \text{or} \quad \dot{m}(h_1 - h_2) = \dot{m}_f(h_1 - h_f)$$

- Defining yield, $Y = \frac{\dot{m}_f}{\dot{m}} = \frac{h_1 - h_2}{h_1 - h_f}$ and combining with compression work gives:

$$\frac{\dot{W}_c}{\dot{m}_f} = \frac{\dot{W}_c}{\dot{m}Y} = [T_1(s_1 - s_2) - (h_1 - h_2)] \left(\frac{h_1 - h_f}{h_1 - h_2} \right)$$



Simple Linde-Hampson (JT) Refrigerator



- Applying 1st law (energy balance) to everything except the compressor gives:

$$\dot{Q}_c = \dot{m}(h_1 - h_2) = \dot{m}y\Delta h_{fg}$$

- Combining with the expression for the compressor work provides an equation for the COP:

$$COP = \frac{\dot{Q}_c}{\dot{W}} = \frac{(h_1 - h_2)}{[T_1(s_1 - s_2) - (h_1 - h_2)]}$$

- Comparing with the Carnot COP gives the FOM (or % of Carnot):

$$FOM = \frac{(h_1 - h_2)(T_1 - T_c)}{[T_1(s_1 - s_2) - (h_1 - h_2)]T_c}$$

Example: Linde-Hampson w/ Argon

- Performance at 20 MPa:

- $h_1 = 349 \text{ J/g}$
 - $h_2 = 315 \text{ J/g}$
 - $s_1 = 3.88 \text{ J/g}\cdot\text{K}$
 - $s_2 = 2.7 \text{ J/g}\cdot\text{K}$

$$COP = \frac{(34 \text{ J/g})}{[(300 \text{ K})(1.18 \text{ J/g}\cdot\text{K}) - 34 \text{ J/g}]} = 0.1063$$

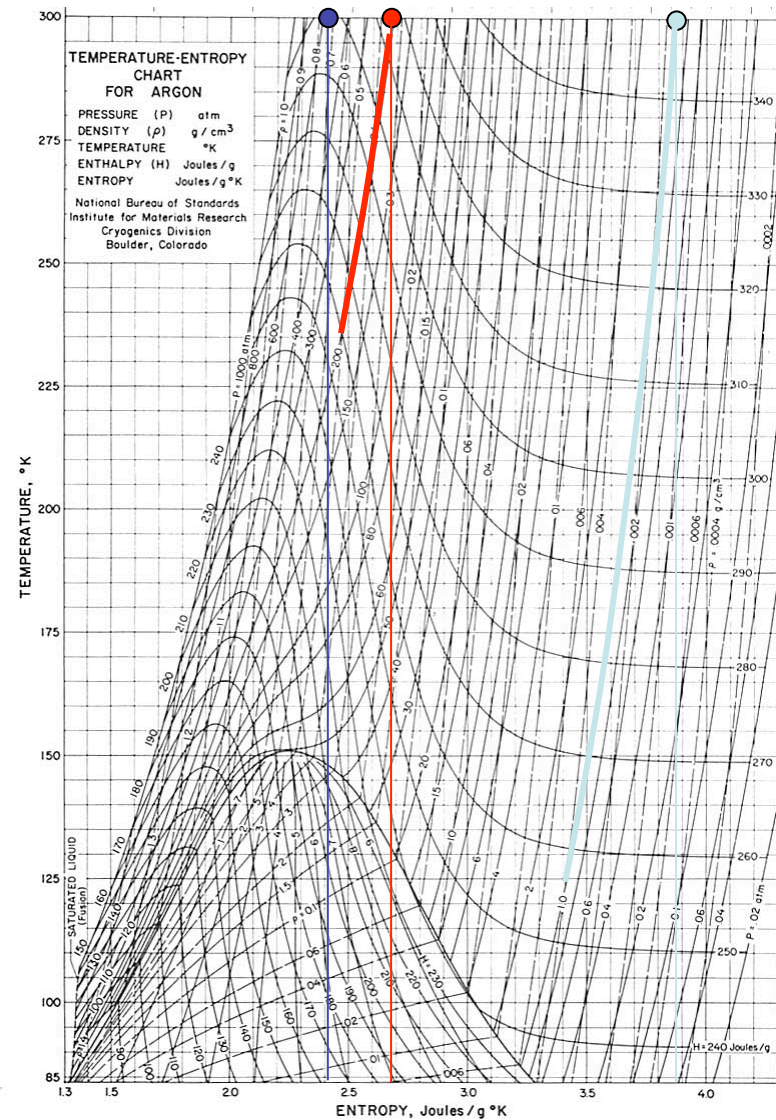
$$FOM = \frac{(34 \text{ J/g})(300 - 87.28 \text{ K})}{[(300 \text{ K})(1.18 \text{ J/g}\cdot\text{K}) - 34 \text{ J/g}](87.28 \text{ K})} = 0.259$$

- Performance at optimized P

- $h_2 = 298 \text{ J/g}$
 - $s_2 = 2.4 \text{ J/g}\cdot\text{K}$

$$COP = \frac{(51 \text{ J/g})}{[(300 \text{ K})(1.48 \text{ J/g}\cdot\text{K}) - 51 \text{ J/g}]} = 0.1298$$

$$FOM = \frac{(51 \text{ J/g})(300 - 87.28 \text{ K})}{[(300 \text{ K})(1.48 \text{ J/g}\cdot\text{K}) - 51 \text{ J/g}](87.28 \text{ K})} = 0.316$$



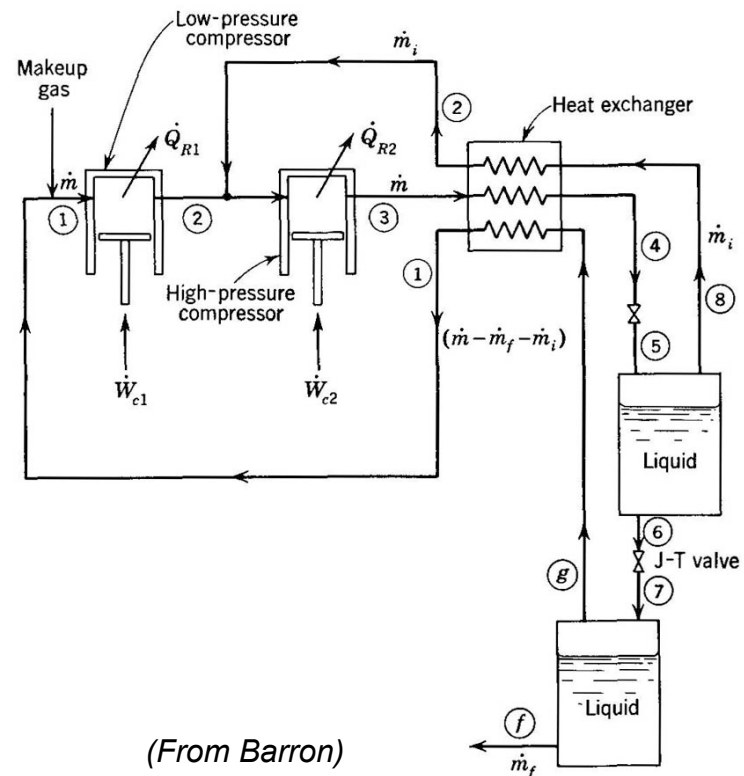
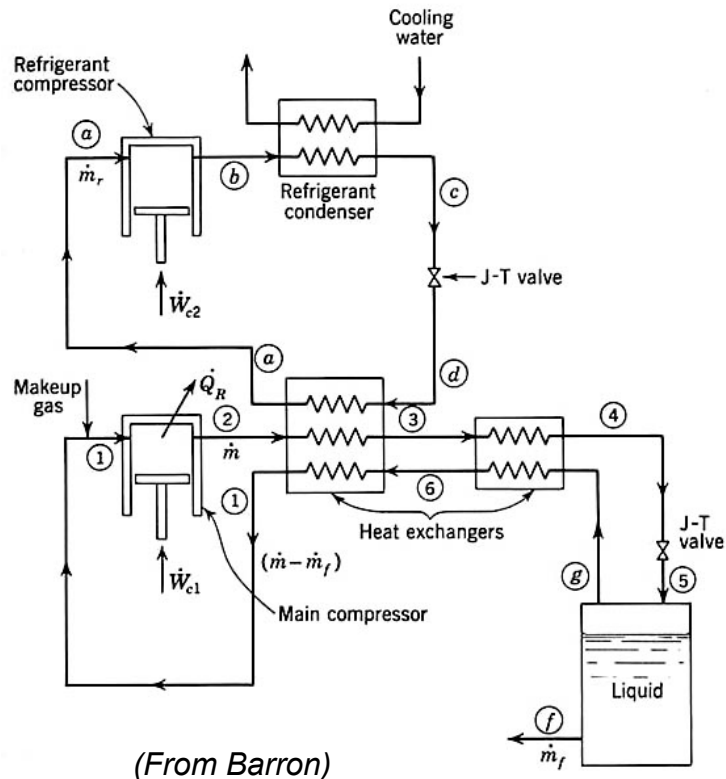
Linde-Hampson Performance

- Optimum theoretical performance realized by minimizing h_2 (P_2 such that h is on the inversion curve)
- P_2 is typically ~ 100 atm.
- Theoretical performance with $P_2 = 20$ atm.(from Barron):

Table 3.3. Performance of the Linde-Hampson system using different fluids. $p_1 = 101.3$ kPa (14.7 psia); $p_2 = 20.265$ MPa (200 atm); $T_1 = T_2 = 300$ K (80°F); heat-exchanger effectiveness = 100 percent; compressor overall efficiency = 100 percent

Fluid	Normal Boiling Point		Liquid Yield $y = \dot{m}_l/\dot{m}$	Work per Unit Mass Compressed		Work per Unit Mass Liquefied		Figure of Merit FOM = \dot{W}_l/\dot{W}
	K	°R		kJ/kg	Btu/lb _m	kJ/kg	Btu/lb _m	
N ₂	77.36	139.3	0.0708	472.5	203.2	6673	2869	0.1151
Air	78.8	142	0.0808	454.1	195.2	5621	2416	0.1313
CO	81.6	146.9	0.0871	468.9	201.6	5381	2313	0.1428
A	87.28	157.1	0.1183	325.3	139.8	2750	1182	0.1741
O ₂	90.18	162.3	0.1065	405.0	174.1	3804	1636	0.1671
CH ₄	111.7	201.1	0.1977	782.4	336.4	3957	1701	0.2758
C ₂ H ₆	184.5	332.1	0.5257	320.9	138.0	611	262	0.5882
C ₃ H ₈	231.1	416.0	0.6769	159.0	68.4	235.0	101.0	0.5976
NH ₃	239.8	431.6	0.8079	363.1	156.1	449.4	193.2	0.7991

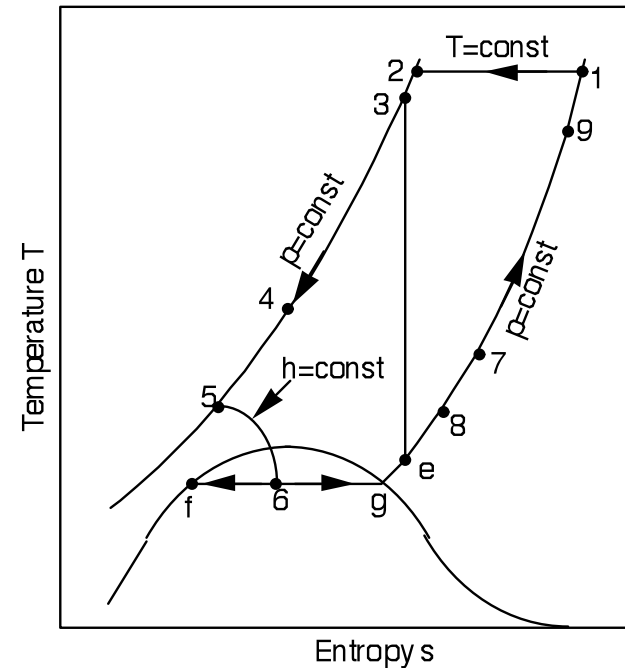
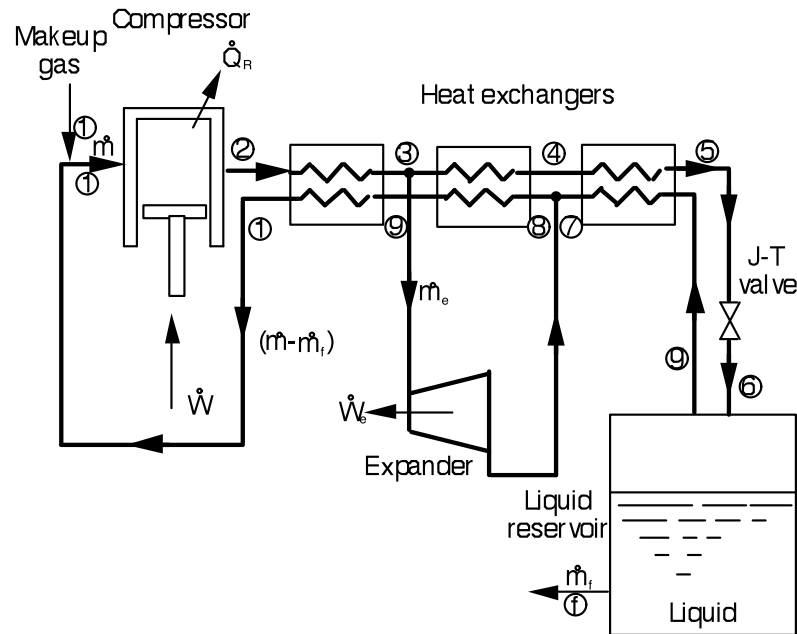
Linde-Hampson Cycle Enhancements



- Pre-cooled L-H cycle
 - Optimize performance via pressure, pre-cooling temperature and mass flow ratio
 - FOM increased by ~ factor of 2

- Dual-pressure L-H cycle
 - Optimize performance via two pressures and fractional mass flow ratio
 - FOM increased by ~ factor of 1.9

Claude Cycle: isentropic expansion



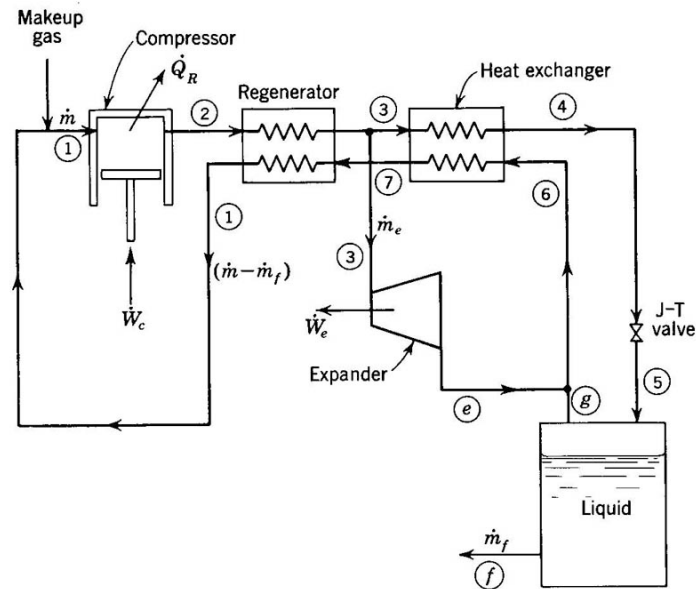
- Isentropic expansion, characterized by $\mu_s = dT/dP_s$ (always >0) results in larger temperature drop for a given pressure drop than with isenthalpic expansion
- 1st and 2nd law analyses give:

$$y = \left(\frac{h_1 - h_2}{h_1 - h_f} \right) + x \left(\frac{h_3 - h_e}{h_1 - h_f} \right); \quad x = \frac{\dot{m}_e}{\dot{m}}; \quad x + y < 1$$

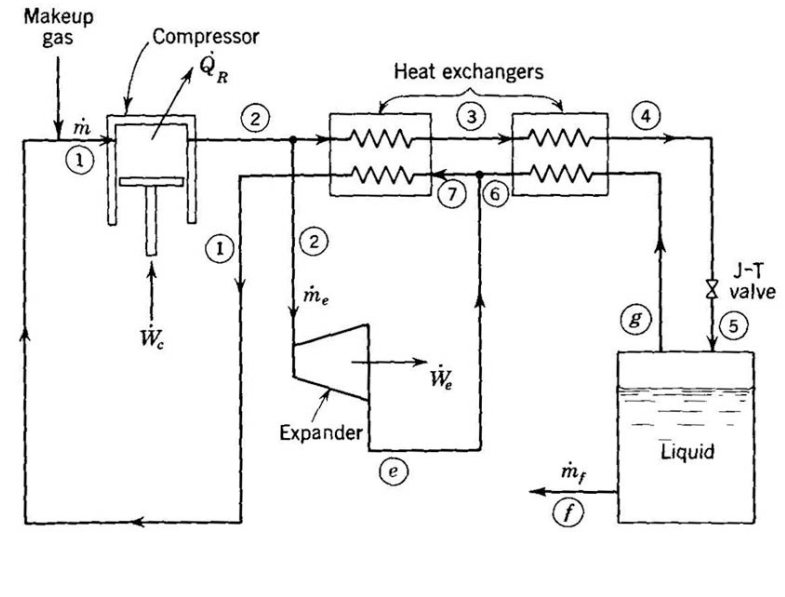
$$\frac{\dot{W}_{net}}{\dot{m}_f} = \frac{[T_1(s_1 - s_2) - (h_1 - h_2) - x(h_3 - h_e)](h_1 - h_f)}{[(h_1 - h_2) + x(h_3 - h_e)]}$$

Optimize performance by varying P_2 , T_3 , and x .

Claude Cycle: Variations



(From Barron)

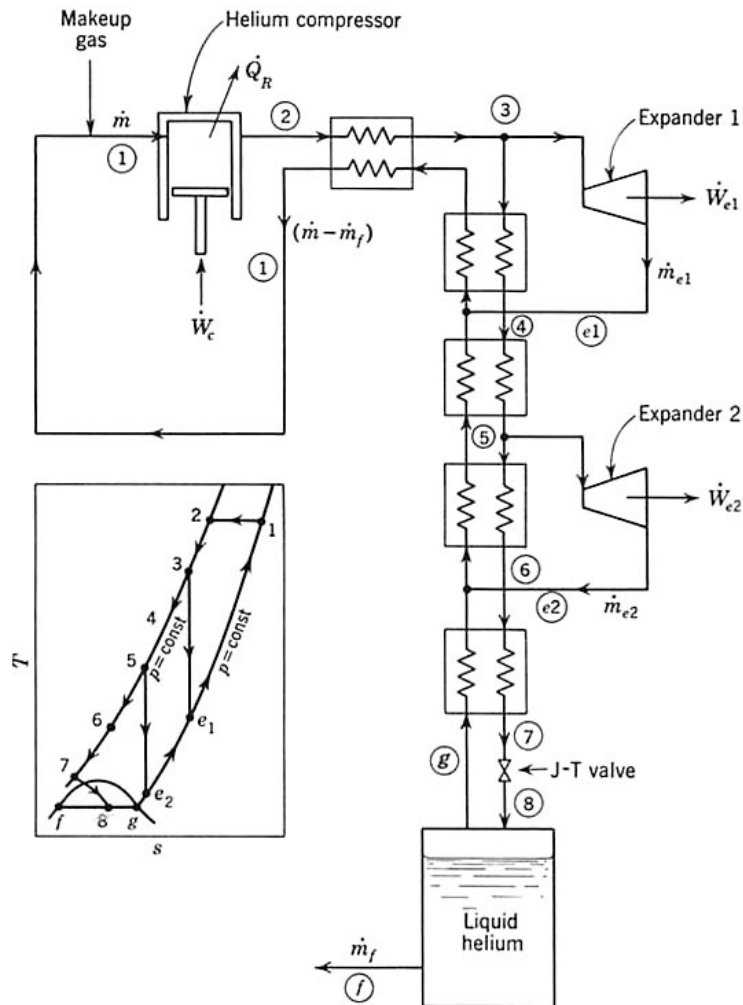


(From Barron)

- Kapitzka cycle
 - Low pressure (7 atm) production of liquid air
 - Regenerative heat exchanger

- Heylandt cycle
 - High pressure (200 atm) air liquefaction
 - Room temperature expander

Collins Liquefier

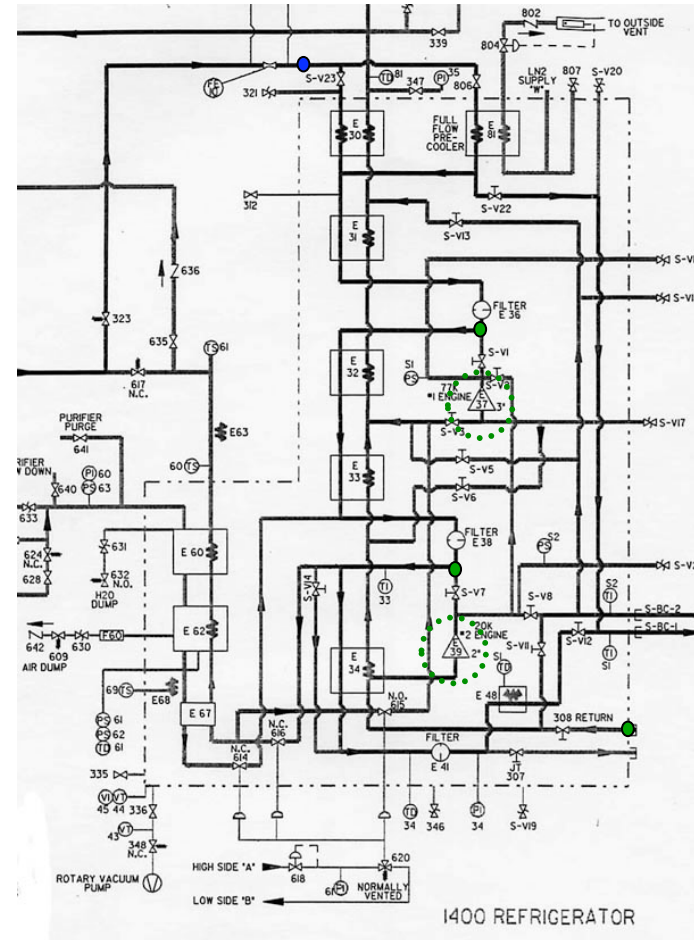


- Introduced by Sam Collins (MIT) in 1952
- Optimized performance via expander flow rates and temperatures
- LN₂ pre-cooling increases yield by factor of 3.

(From Barron)

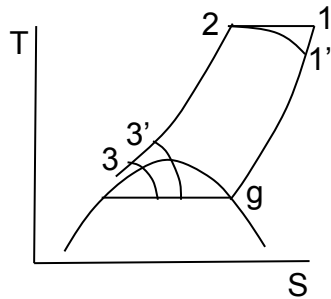
Commercial Helium Liquefier

- The dashed line encloses the 'cold box,' i.e. everything except the compressor.
- Find the expansion engines
- Trace the flow from LN₂ precooler through the cold box to the JT valve.



Influence of Non-Ideal Components

- A non-ideal heat exchanger will have an effectiveness less than 1.



$$\varepsilon = \frac{h_{1'} - h_g}{h_1 - h_g}$$

$$\eta_c = \frac{\left(\frac{\dot{W}}{\dot{m}}\right)_{\text{isothermal}}}{\left(\frac{\dot{W}}{\dot{m}}\right)_{\text{actual}}}$$

- A non-isothermal compressor will require more work than an isothermal compressor

- The influence of these non-ideal parameters on the cooling capacity (refrigerator), liquid yield (liquefier), and compression work for a simple Linde-Hampson system is:

$$\frac{\dot{Q}}{\dot{m}} = (h_1 - h_2) - (1 - \varepsilon)(h_1 - h_g)$$

$$y = \frac{h_{1'} - h_2}{h_{1'} - h_f} = \frac{(h_1 - h_2) - (1 - \varepsilon)(h_1 - h_g)}{(h_1 - h_f) - (1 - \varepsilon)(h_1 - h_g)}$$

$$\frac{\dot{W}}{\dot{m}} = \frac{1}{\eta_c} \left[T_1 (s_{1'} - s_2) - (h_1 - h_2) + (1 - \varepsilon)(h_1 - h_g) \right]$$

