Thermodynamics for Cryogenics

with the emphasis here on large-scale helium cryogenics

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June, 2019

Outline

- Definitions
- Perfect gas (Pv=RT)
- Equations of state
- Entropy
- Compression and expansion processes
- Liquid/vapor systems

Old science with modern applications

- Thermodynamics is the study of macroscopic energy transformations between heat and work
- Thermodynamics has its basis in attempts to understand combustion and steam power (much in the 19th century) but is still "state of the art" in terms of practical engineering issues for cryogenics

James Dewar (invented vacuum flask in 1892)

Focus of this lecture

- Thermodynamics is a large area of study, far too much to cover in this one-hour introduction
- I will focus on the thermodynamics concepts which I have found most important in my experience designing cryogenic systems and cryostats

The laws of thermodynamics

- First law – “The energy of the isolated system is conserved.” (Conservation of energy)
- Second law – “The entropy of the isolated system increases in all real processes and is conserved in reversible (theoretical) processes.”
- Third law – “The entropy of a pure substance in complete thermodynamic equilibrium becomes zero at a temperature of absolute zero.” (One can never reach absolute zero.)

Some thermodynamics definitions

- A "system" in thermodynamics is a specified region in which mass transfer and/or heat transfer is studied
  - A "boundary" separates the system from its "surroundings"
  - Proper definition of the system can be important in solving a problem (we'll see that in some examples later)

More definitions

- An “isolated” system has no mass or energy crossing the boundary
- A “closed” system has no mass crossing the boundary
- An “open” system has mass crossing the boundary and may or may not have constant mass
- The thermodynamic “state” of the system is the condition at a moment in time as defined by the system properties
- In general, two properties define the state of a system consisting of a pure substance in equilibrium

Commonly used properties

- T – temperature
- P – pressure (force per unit area)
- v – specific volume (volume V per unit mass)
- U – internal energy of the closed system or
- u – internal energy per unit mass
- H – enthalpy = U + PV
- h – enthalpy per unit mass (specific enthalpy)
- S – entropy
- s – entropy per unit mass

Derived properties, C_v , C_p , k

- Some important thermodynamic properties are defined from others, such as the heat capacities, c_v , and c_P , and k

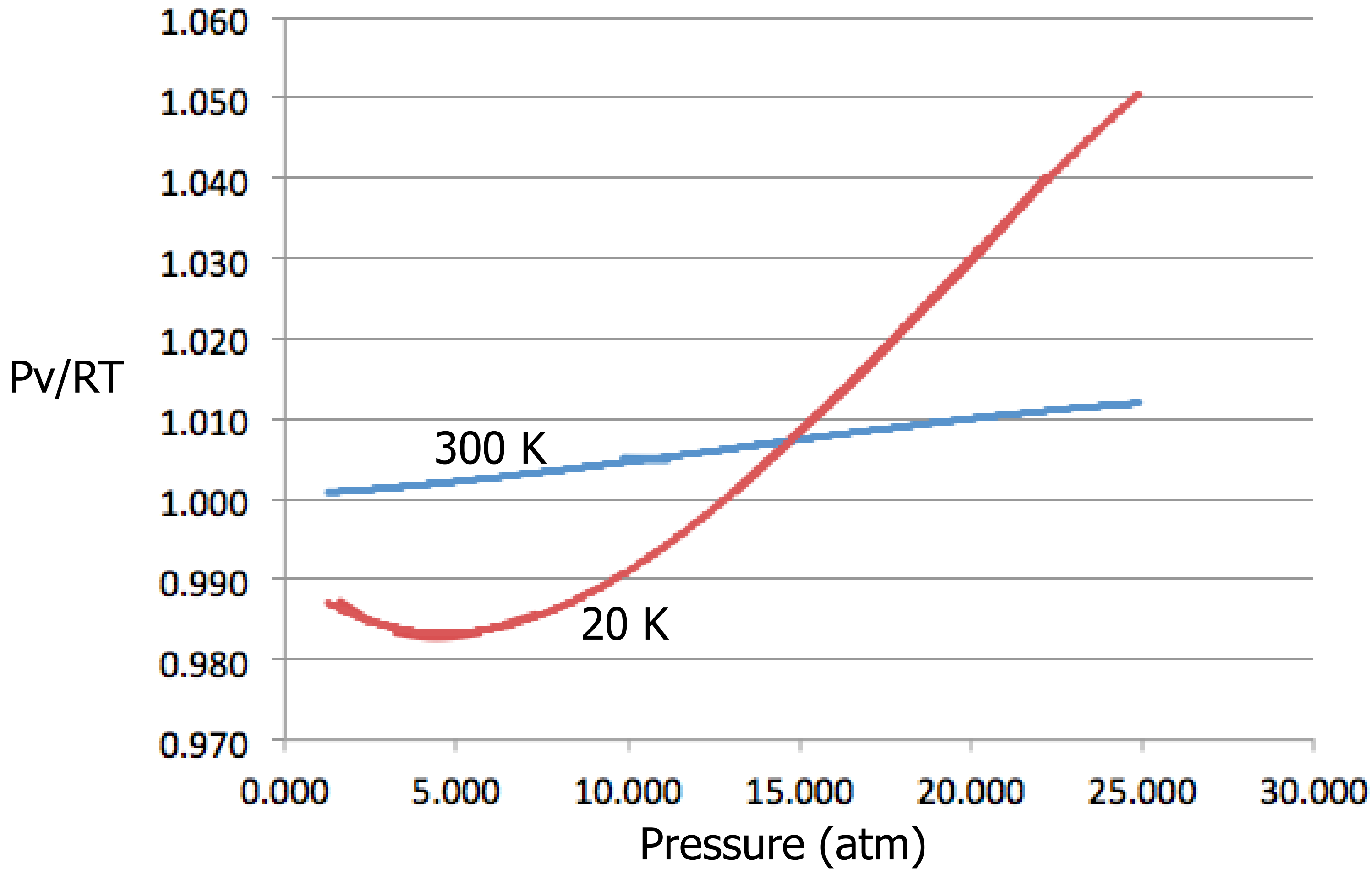
$$c_v \equiv \left.\frac{\partial U}{\partial T}\right)_V \qquad c_p \equiv \left.\frac{\partial H}{\partial T}\right)_P \qquad k \equiv \frac{c_P}{c_v}$$

- Since typically two properties define the state of the pure fluid in thermodynamics, equations generally have two independent variables
- Derivatives then are partial derivatives with respect to one independent variable with the other held constant

Perfect gas approximation

- A perfect gas obeys the equation Pv=RT where R is a constant called the gas constant
- The internal energy of a perfect gas is a function of temperature alone, $\Delta u = c_v \Delta T$ where c_v is constant
- Since h = u +Pv, so h = u + RT for a perfect gas, enthalpy is also a function of temperature alone for a perfect gas, $\Delta h = c_p \Delta T$ where c_p is constant.

Pv/RT versus P for helium



Equations of State

- In many cases, Pv=RT may be a good approximation
  - For example, far enough from the critical pressure and from the condensation temperature
  - Good to within 10% for helium down to 8 K
- Terms may be added to account for deviations from Pv=RT, such as

$$\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots.$$

- This is called the "virial equation", and the coefficients B, C, etc. are called "virial coefficients".
- Equations of state enable calculation of fluid properties based on measurements of some of the basic properties

Helium phase diagram

(Steven W. VanSciver, Helium Cryogenics, p. 54)

- Critical point is 5.2 K, 2.245 atm
- Lambda transition from helum I to helium II is 2.172 K

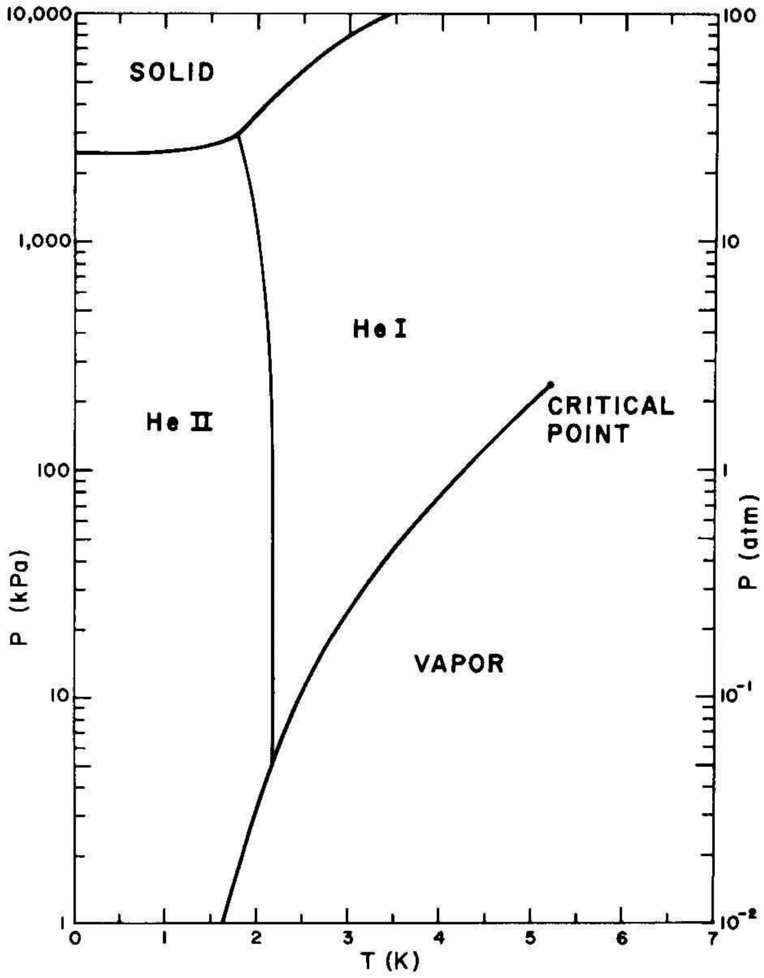


Fig. 3.1. ^{4}He phase diagram.

From Obert, Concepts of Thermodynamics

Point *c* is called the *critical point* and marks the termination of any distinction between liquid and gaseous phases. If liquid-vapor phases in equilibrium at *uv* and confined in a glass cylinder are maintained in equilibrium while the temperature and pressure are raised, the attainment of state *c* will be marked by the disappearance of the meniscus that identified the presence of two phases. In the vicinity of state *c*, the properties of the liquid phase and the vapor phase approach each other in similarity; for example, the specific volumes of liquid and gas approach the same value. At state *c*, all properties of both phases become identical. Note that a single phase of a fluid when confined in a glass container could not be visually recognized to be a solid, liquid, or gas (unless a change in color occurs with change of phase).

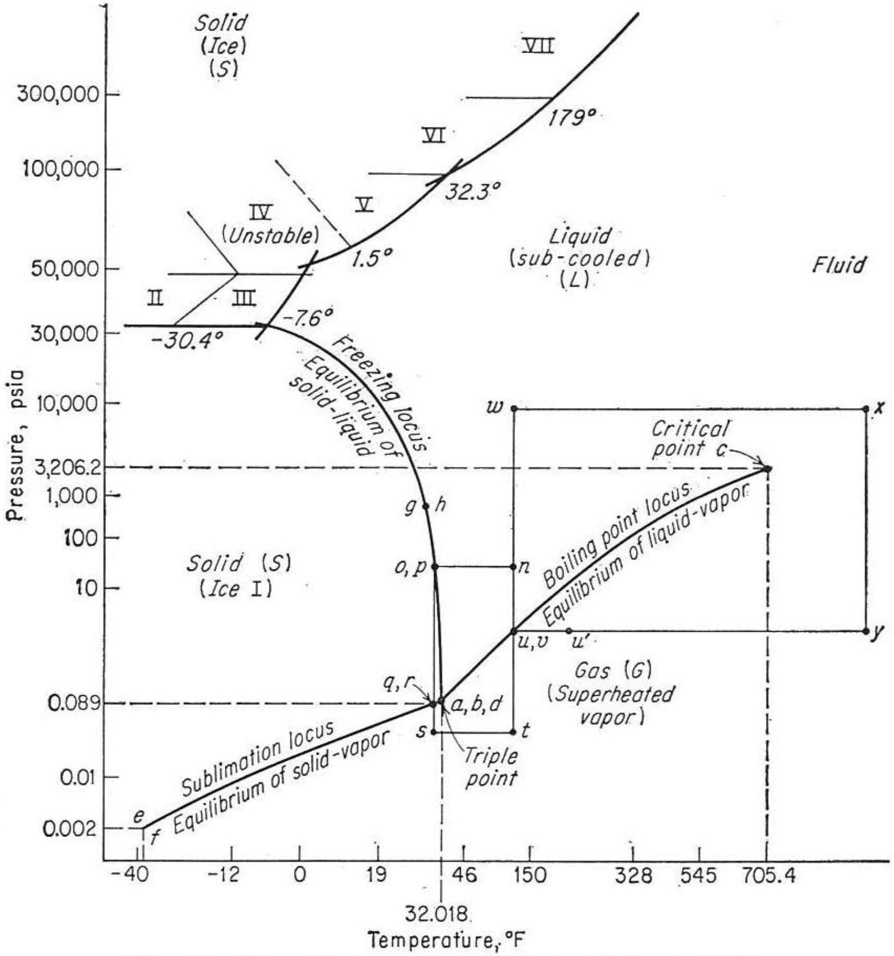


FIG. 9-2. Phase diagram for water (not entirely to scale).

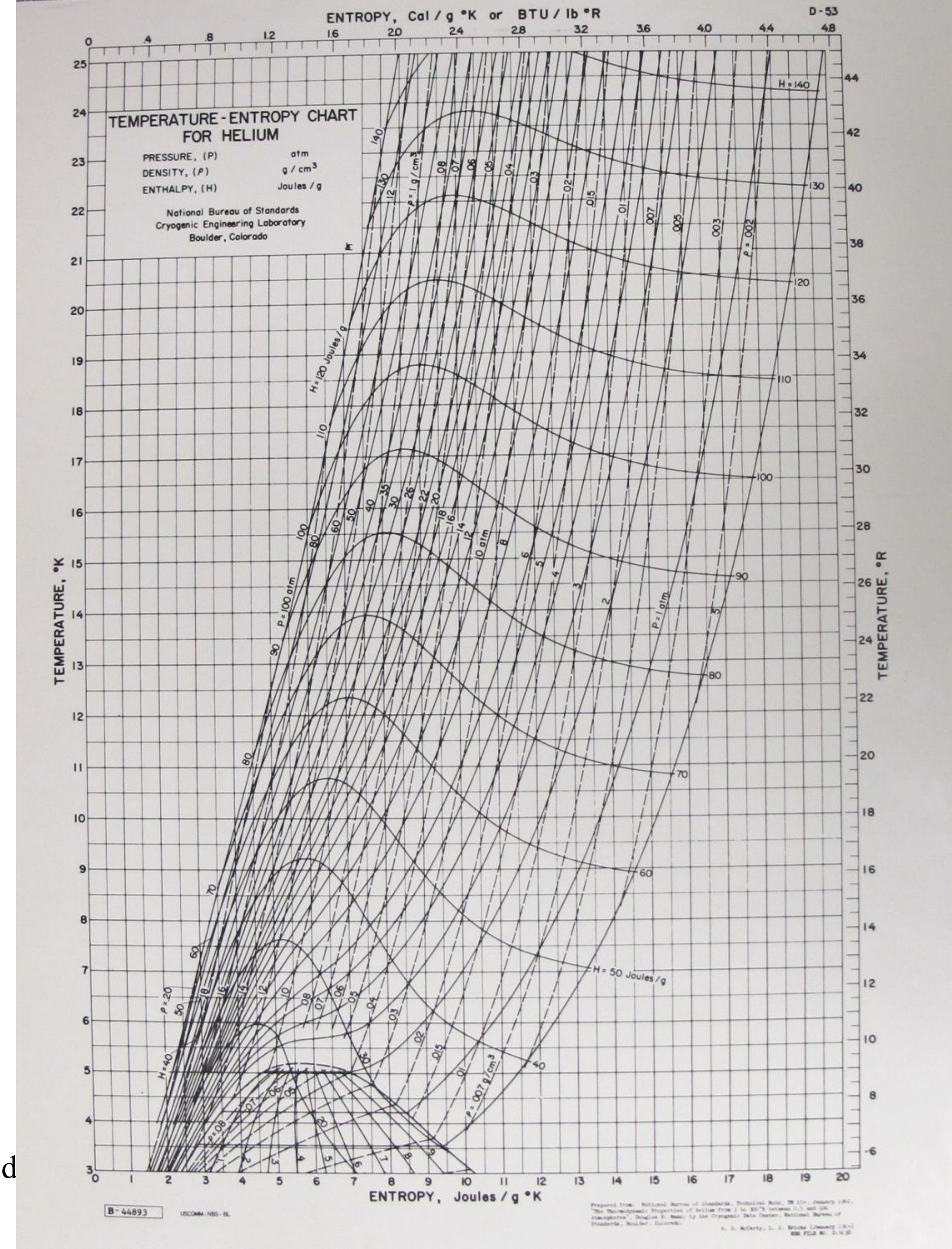
Entropy

- Least intuitive of the common properties
- Definition of entropy is based on energy change in a perfect, loss-free (reversible) process

$$dS = \frac{dQ_{rev}}{T}$$

- Entropy is the property which is held constant in a adiabatic (no heat flow in or out) reversible process like the perfect closed piston compression and expansion

T-s diagram for helium



The TdS equations

- From the first law (energy conservation) for a closed system with reversible addition or removal of heat and mechanical work (pdV), we have:

$$dQ_{rev} = dU + PdV$$

- With $dQ_{rev} = TdS$ we have the first TdS equation:

$$TdS = dU + PdV$$

- From $H = U + PV \quad dH = dU + PdV + VdP$
- Which gives us the second TdS equation:

$$TdS = dH - VdP$$

Isothermal compression

Example application of TdS equation

- From the second TdS equation, $TdS = dH - VdP$

with constant temperature (isothermal) compression of an ideal gas, dH = 0, so $TdS = -VdP$

- For the ideal gas, $PV = RT = const$
- substituting $V = RT/P$ gives

$TdS = -RT\dfrac{dP}{P}$ and integrating,

$$T\Delta s = RT \times \ln\left(P_{out}/P_{in}\right)$$

Isothermal compression

- Isothermal compression “squeezes” the entropy out of the helium by increasing pressure at constant temperature
- Enthalpy h (function of T alone) remains constant
- Yet energy (heat) is removed in isothermal compression
- That energy is $\Delta Q = T\Delta s$ and is equal to the compressor work, which we saw is $T\Delta s = RT \times \ln\left(P_{out} / P_{in}\right)$

Isothermal compression example

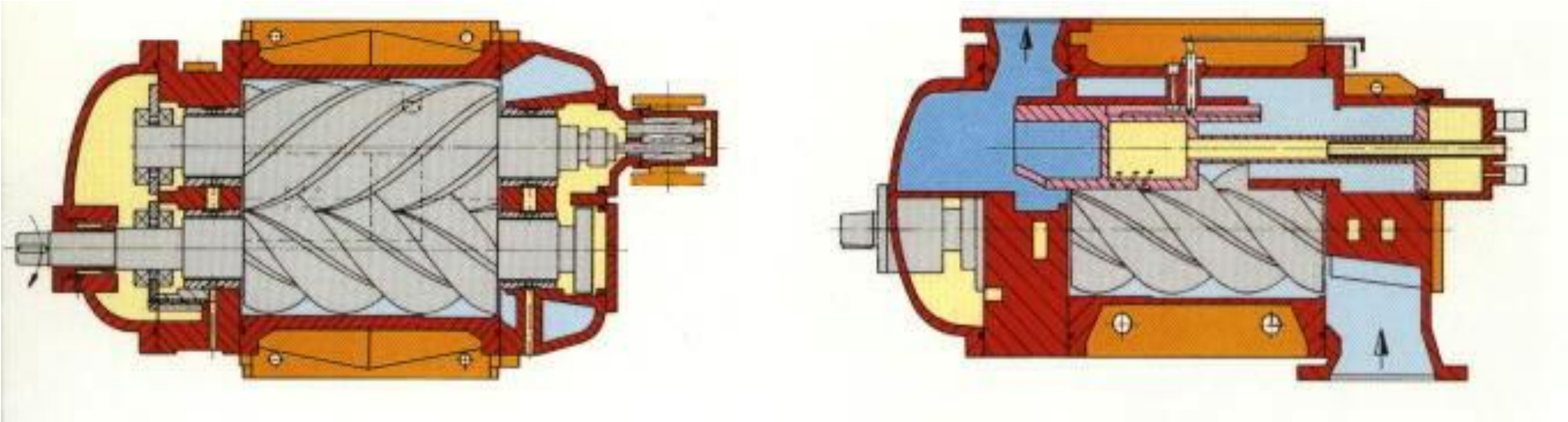
- The second stage screw compressor at Fermilab's MTF compresses 200 grams/sec helium from about 2.6 bar to 15 bar
- For helium R = 2.078 J/gK, so the ideal work at 300 K would be

$$\left(2.078\frac{J}{gK}\right)(300K)\ln\left(\frac{15}{2.6}\right)\left(200\frac{grams}{\sec}\right)=220kW$$

- With typical power consumption of 800 HP = 600 kW, the isothermal efficiency is about 37%

A real helium compressor

- Oil-flooded screw compressors are now standard
- A typical pressure ratio is about 4:1, so two stages are used in a typical helium plant to get a 15:1 to 20 :1 pressure ratio



Isentropic expansion

- Removes energy from the system at constant entropy by means of adiabatic (no heat transfer) reversible (loss-free) work
- Expansion at constant entropy from about 70,000 atm and room temperature to 1 atm would remove enthalpy (as work) to that of 2-phase helium

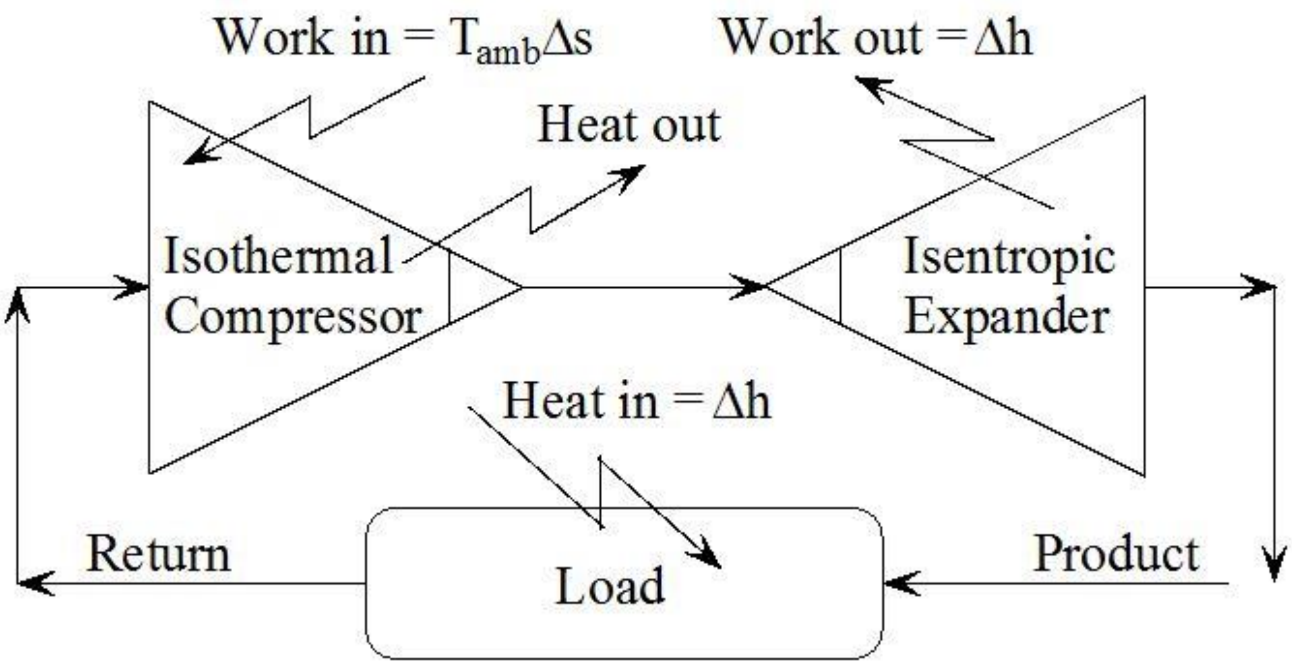
Isentropic efficiency

- Isentropic expansion efficiency is defined as

$$\frac{\Delta h_{real}}{\Delta h_{isentropc}}$$

- where $\Delta h = h_{in} - h_{out}$
- Δh_{real} will always be less than $\Delta h_{isentropc}$ so efficiency will be less than 100%
- For real expanders, 65% to 85%

Ideal helium process



Net ideal work in = $T_{amb}\Delta s - \Delta h$
(in dimension of energy per unit mass)

Isothermal heat absorption

- Net ideal work (energy per unit mass of working fluid) into the system is $T_{amb}\Delta s - \Delta h$
- For a refrigerator with the heat load absorbed by evaporation at constant liquid temperature, T_{liq}, $\Delta h = T_{liq}\,\Delta s$
- Thus, the ratio of applied work to heat absorbed is $(T_{amb}\,\Delta s - \Delta h)/\,\Delta h = T_{amb}/T_{liq} - 1$
- For low temperatures this is approximately the ratio of absolute temperatures, T_{amb}/T_{l}

Power required for a non-isothermal load

- Use $P = \dot{m}\{T_{amb}(s_{out} - s_{in}) - (h_{out} - h_{in})\}$
- Where P is the ideal room-temperature power required to remove a non-isothermal heat load
- I will show the use of this later in calculating cryogenic system power

Exergy

- In many cryogenics analyses, authors describe an "exergy" analysis
  - Exergy is defined as de = dh – T_0ds, which is the quantity described previously as the ideal refrigeration power
  - At each stage, one can compare the real power required with expected, from

$$P = \dot{m}\left\{T_{amb}\left(s_{out} - s_{in}\right) - \left(h_{out} - h_{in}\right)\right\}$$

Gibbs Free Energy

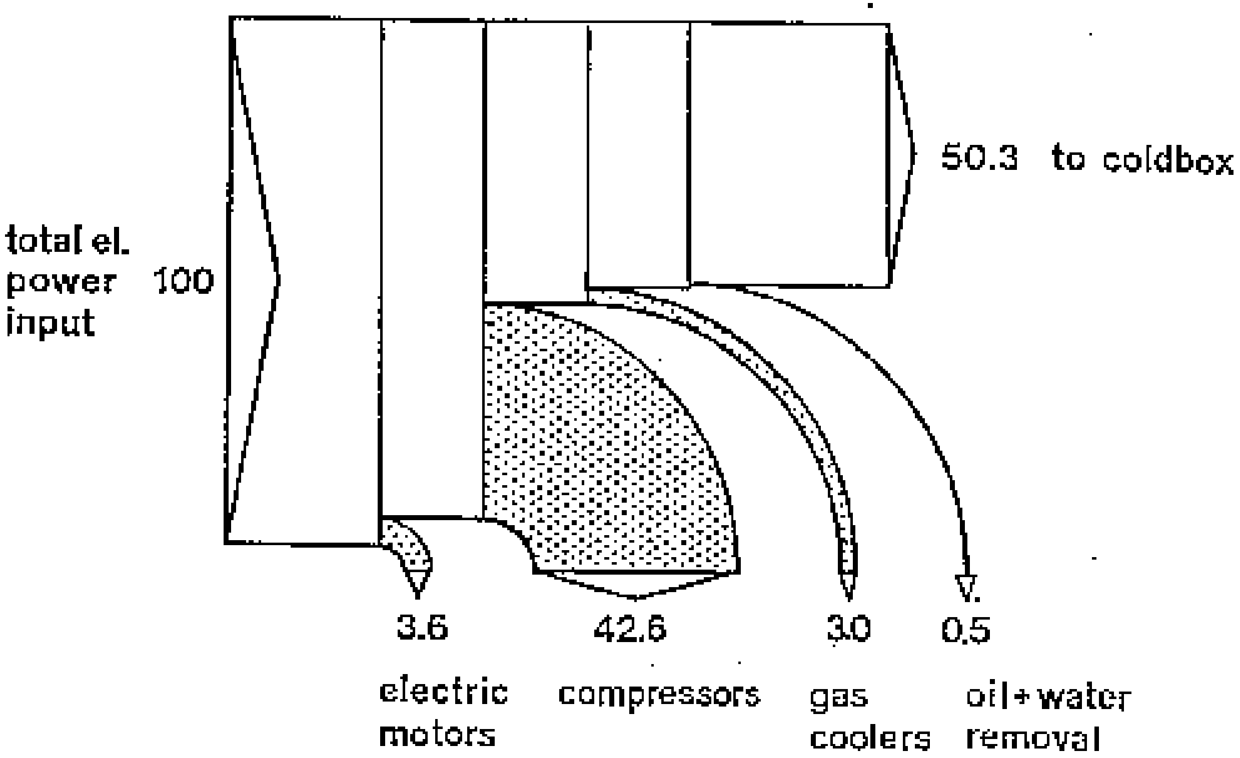
- In thermodynamics texts, you will find the quantity Gibbs Free Energy defined, which is $G = H - TS$
- For processes which start and end at the same temperature, one may compare the real process with an ideal cycle rejecting heat to that reference temperature, T_0. On a per unit mass basis, $dg = dh - T_0 ds$
- So exergy (the ideal work for refrigeration) is basically the same concept in reverse as Gibbs Free Energy, the maximum work that can be extracted from a process doing work

Example cryo power analysis

- See ILCcryoTDP-26June2012.xls

Cryogenic plant losses (compressor)

from B. Ziegler, "Second Law Analysis of the Helium Refrigerators for the HERA Proton Magnet Ring," in Advances in Cryogenic Engineering, Vol. 31, Plenum Press, 1986, p. 693



Cryogenic plant losses (cold box)

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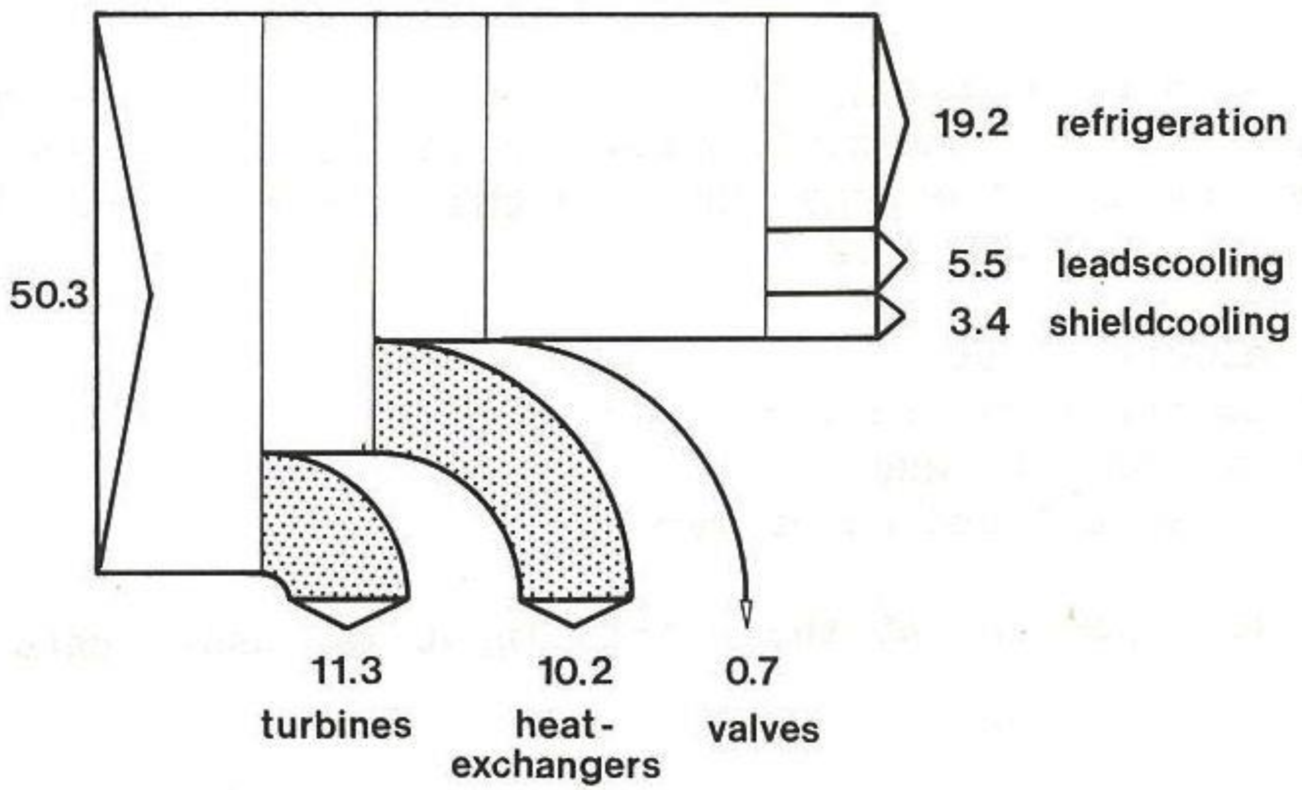
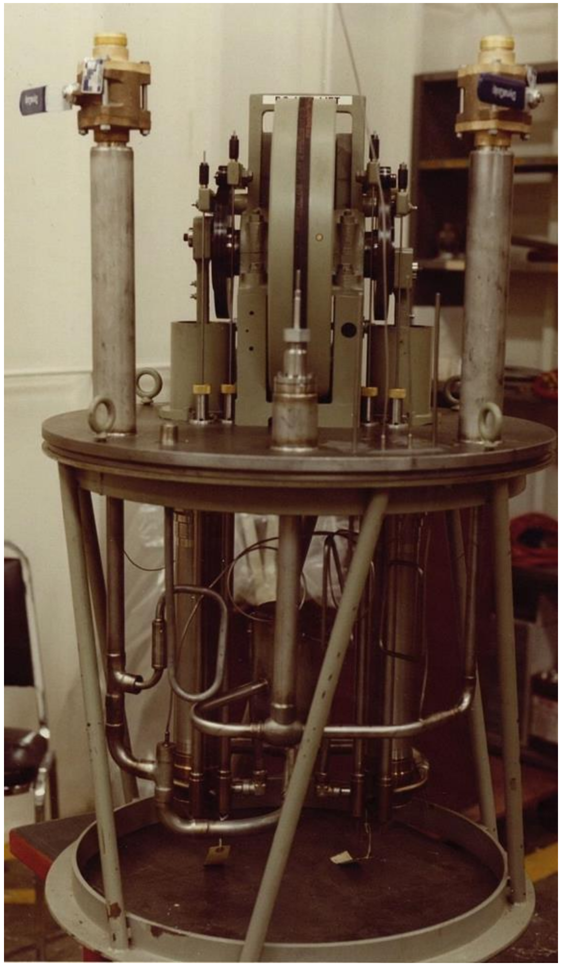


Expansion engines

- Reciprocating expansion engines are used in many small liquefiers and help to illustrate some fundamentals of thermodynamics
- At the right is a Koch Process Systems (similar to "model 1400") expander with cryostat open



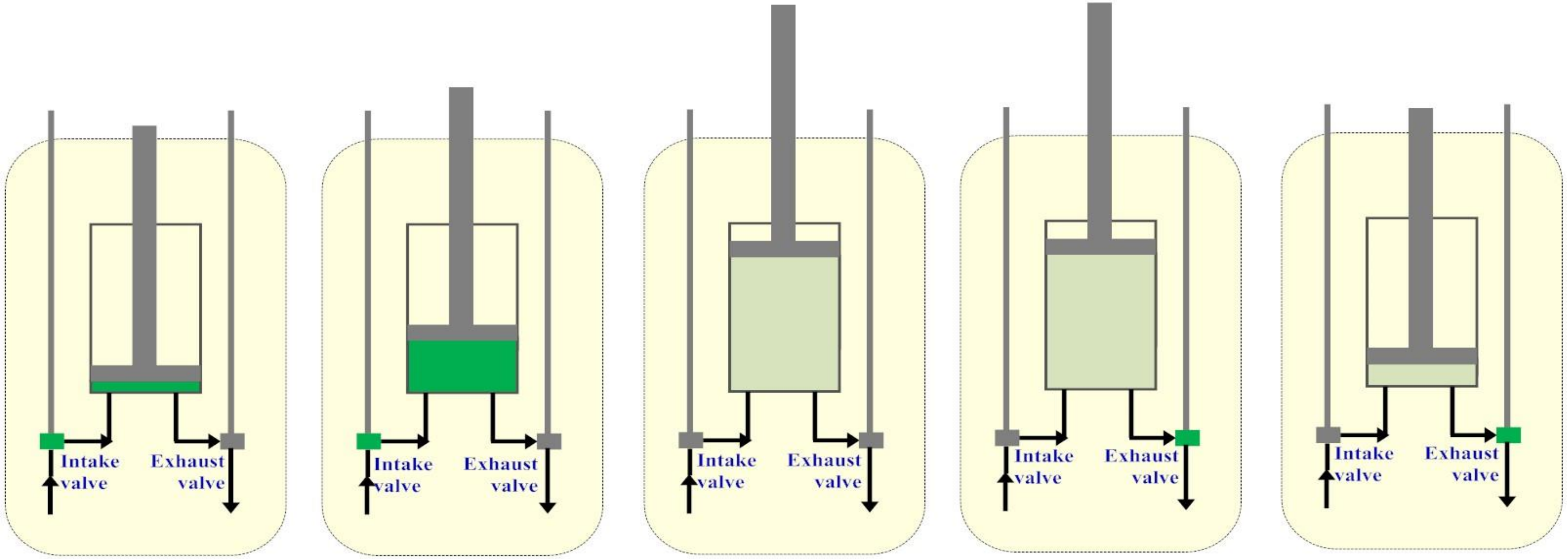
Expansion engine cylinder

- At the right is a close-up of the expander showing the cylinder, valve bodies, and some of the cryogenic piping

Expansion engine cycle

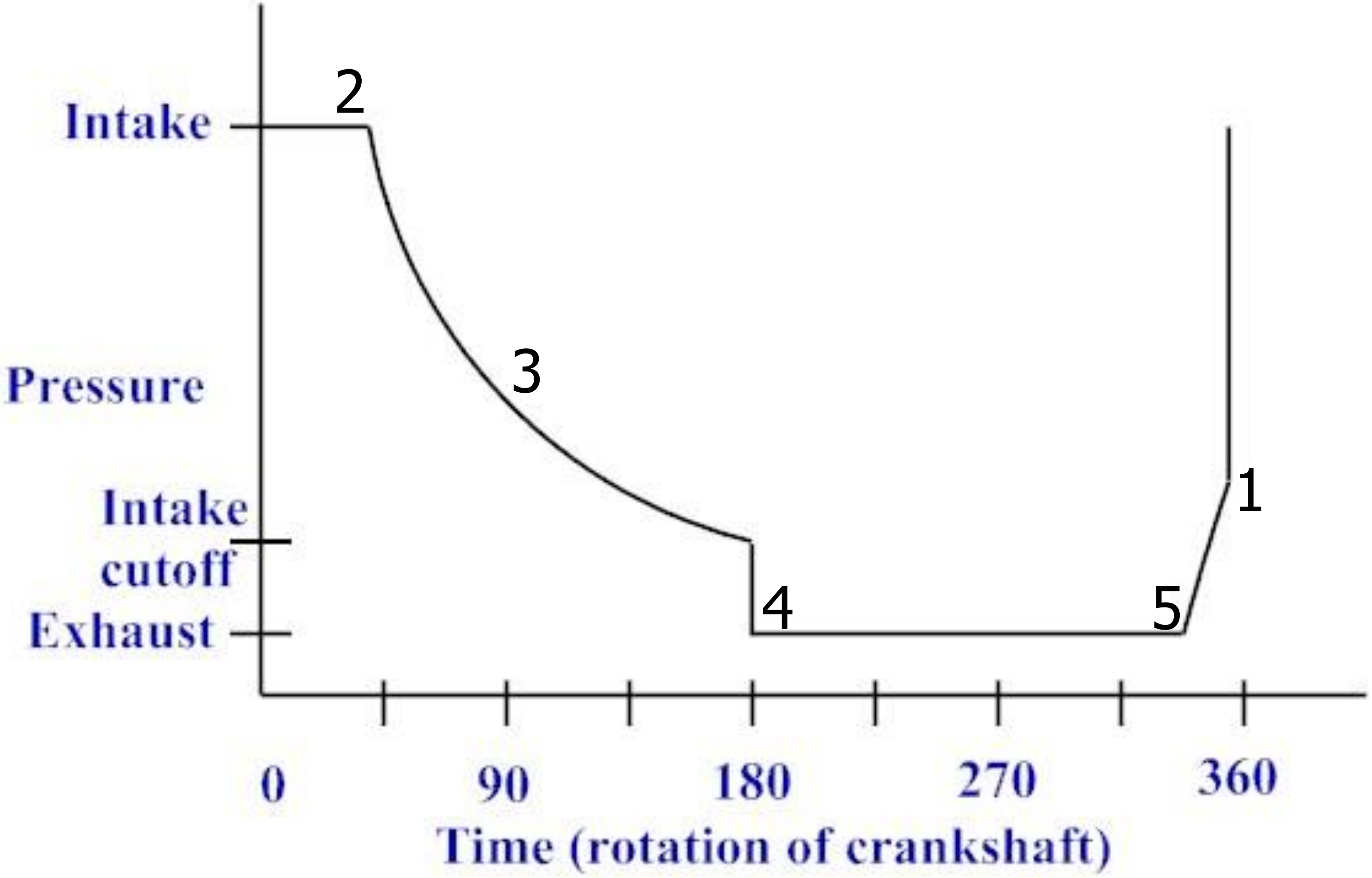
Work extraction Work extraction

1 2 3 4 5



1. Minimal volume, intake valve opens
2. Filling cylinder, then intake valve closes
3. Valves closed, constant mass expansion
4. Maximal volume, exhaust valve opens
5. Cut-off volume, exhaust valve closes

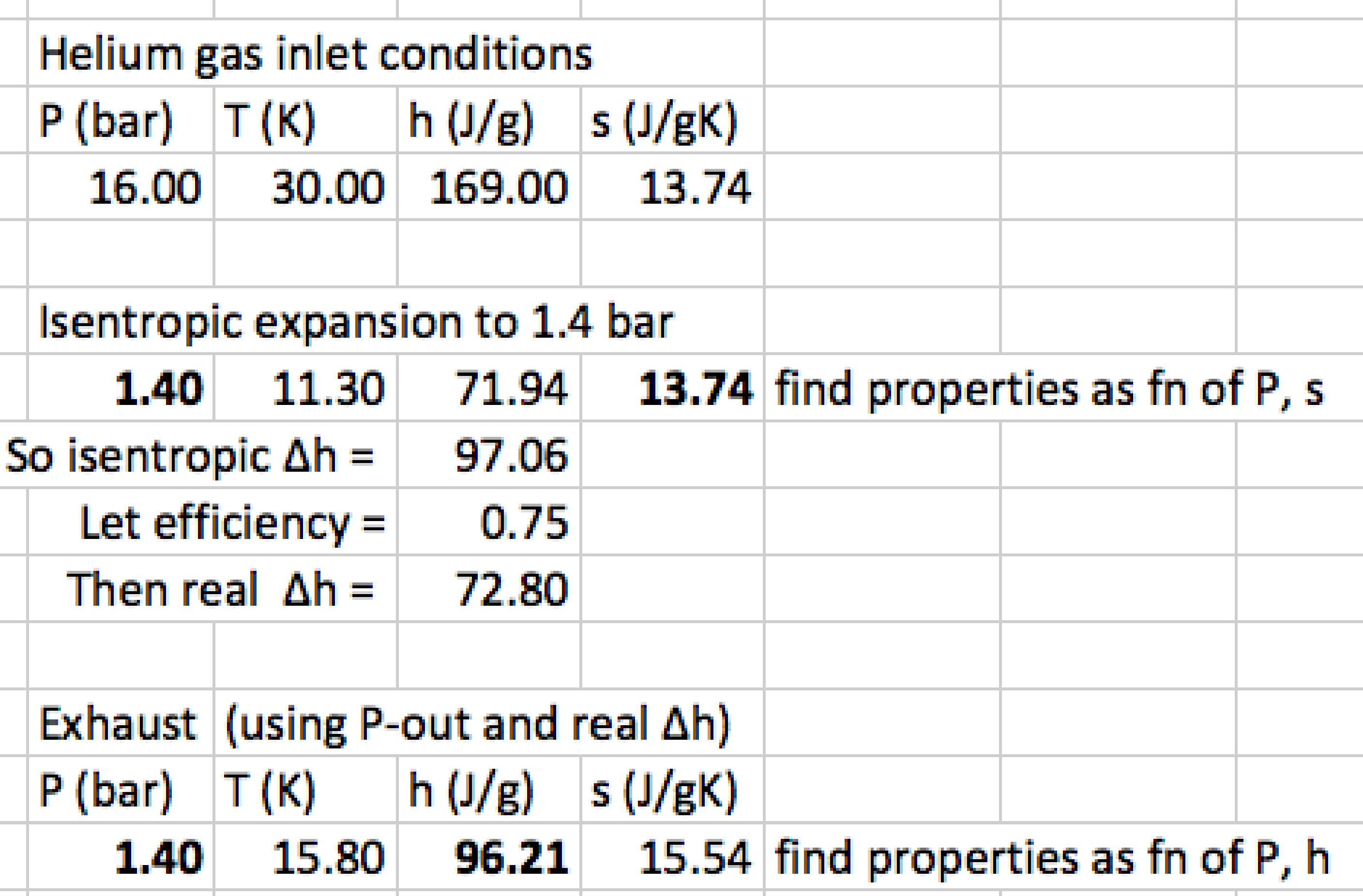
Pressure trace



Efficiency discussion

- Intake cutoff, incomplete expansion
  - Leaves some pressure unutilized
  - Allows larger mass flow (intake valve open longer, more mass into cylinder each stroke)
- Intake and discharge valve leakage
- Heat conduction into expander
- Heat transfer to and from cylinder walls and piston head
- Dead volume leaves cooled helium behind which mixes with intake

Helium expansion example



Helium gas inlet conditions				
P (bar)	T (K)	h (J/g)	s (J/gK)	
16.00	30.00	169.00	13.74	
Isentropic expansion to 1.4 bar				
1.40	11.30	71.94	**13.74**	find properties as fn of P, s
So isentropic Δh =		97.06		
Let efficiency =		0.75		
Then real Δh =		72.80		
Exhaust	(using P-out and real Δh)			
P (bar)	T (K)	h (J/g)	s (J/gK)	
1.40	15.80	**96.21**	15.54	find properties as fn of P, h

Isenthalpic expansion

- Expansion through a valve does no work, and neither adds nor removes energy
  - Process is isenthalpic
- Enthalpy of the perfect gas is a function of temperature alone
  - Isenthalpic process of perfect gas does not change the temperature

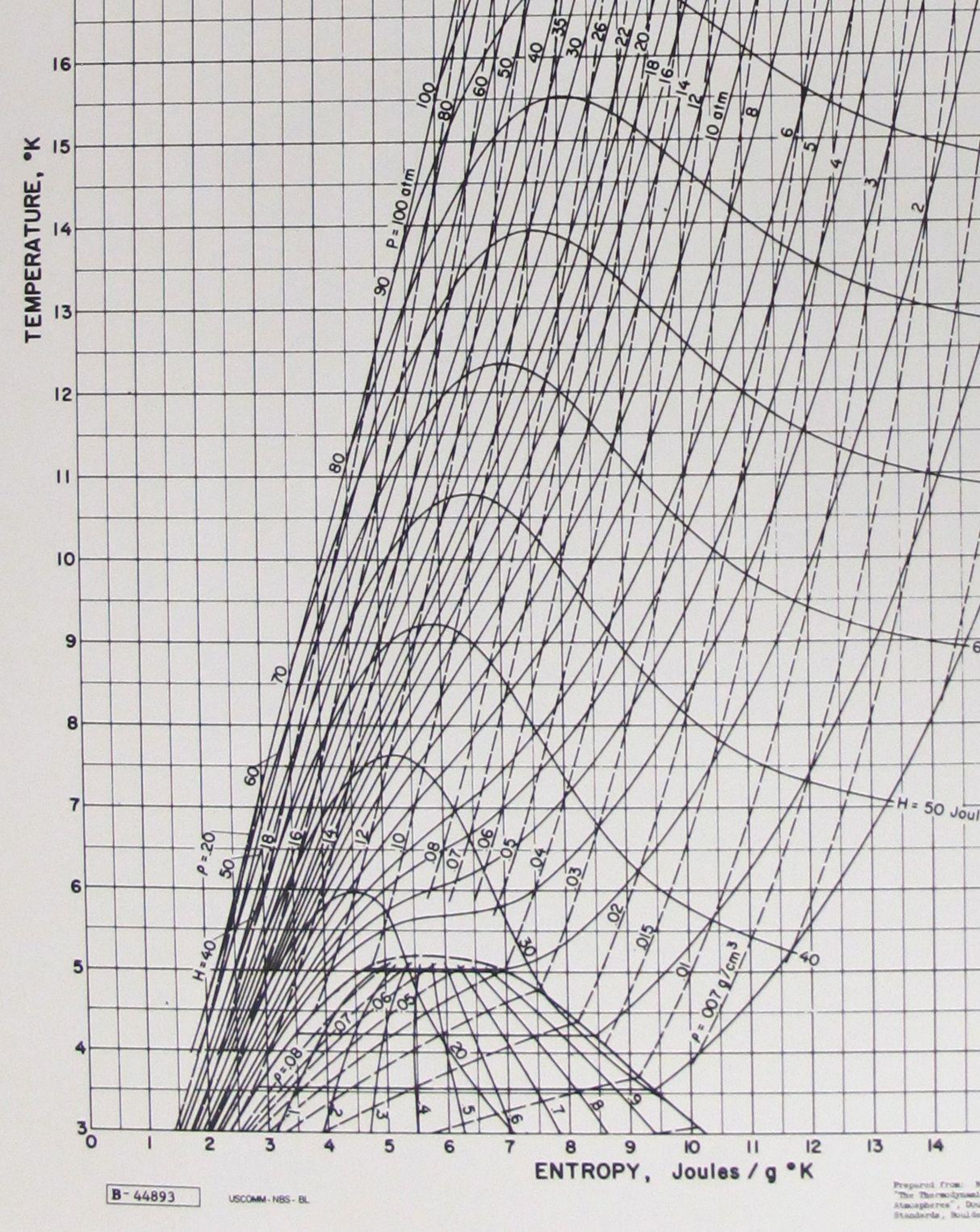
$$\left.\frac{\partial T}{\partial P}\right)_h = 0$$

- Real fluids may change temperature via an isenthalpic expansion
  - Joule-Thomson effect

Joule-Thomson expansion

- In many real fluids, including helium near the liquid-vapor dome (see T-s diagram), isenthalpic expansion may provide temperature drop
  - Not as efficient of isentropic expansion
  - But very convenient and easy (no moving parts)
- Joule-Thomson expansion through a valve is said to be through a "J-T valve"

T-s diagram for helium (closer look)



Helium JT inversion curve

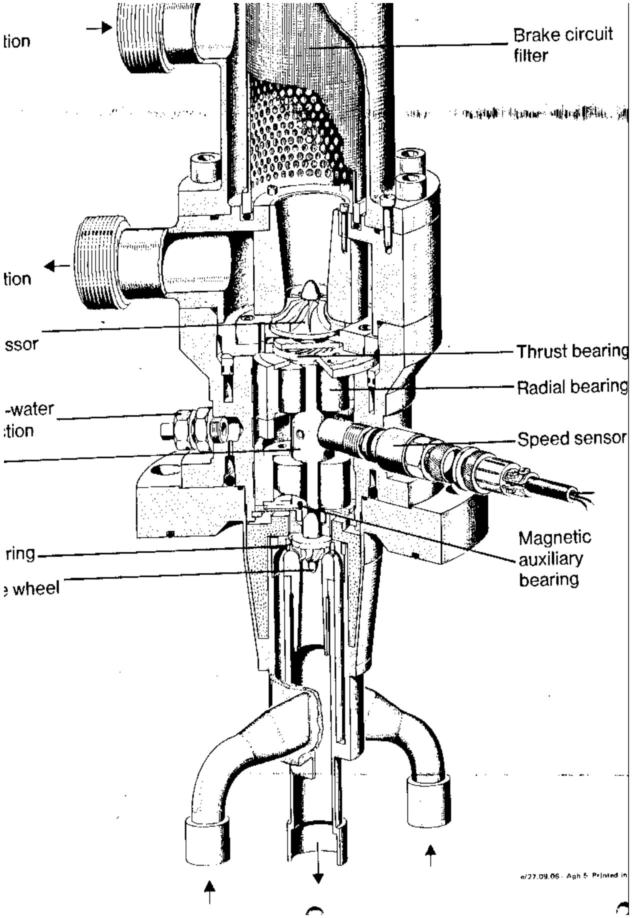
- Note that lines of constant enthalpy are not horizontal (not constant temperature) on the previous T-s diagram.
- Movement along a line of constant enthalpy with a pressure change (isenthalpic expansion or compression) may result in a temperature increase or decrease.

- The curve demarking where $\left.\frac{dP}{dT}\right)_h < 0$ and where $\left.\frac{dP}{dT}\right)_h > 0$

is called the “Joule-Thomson inversion curve”.

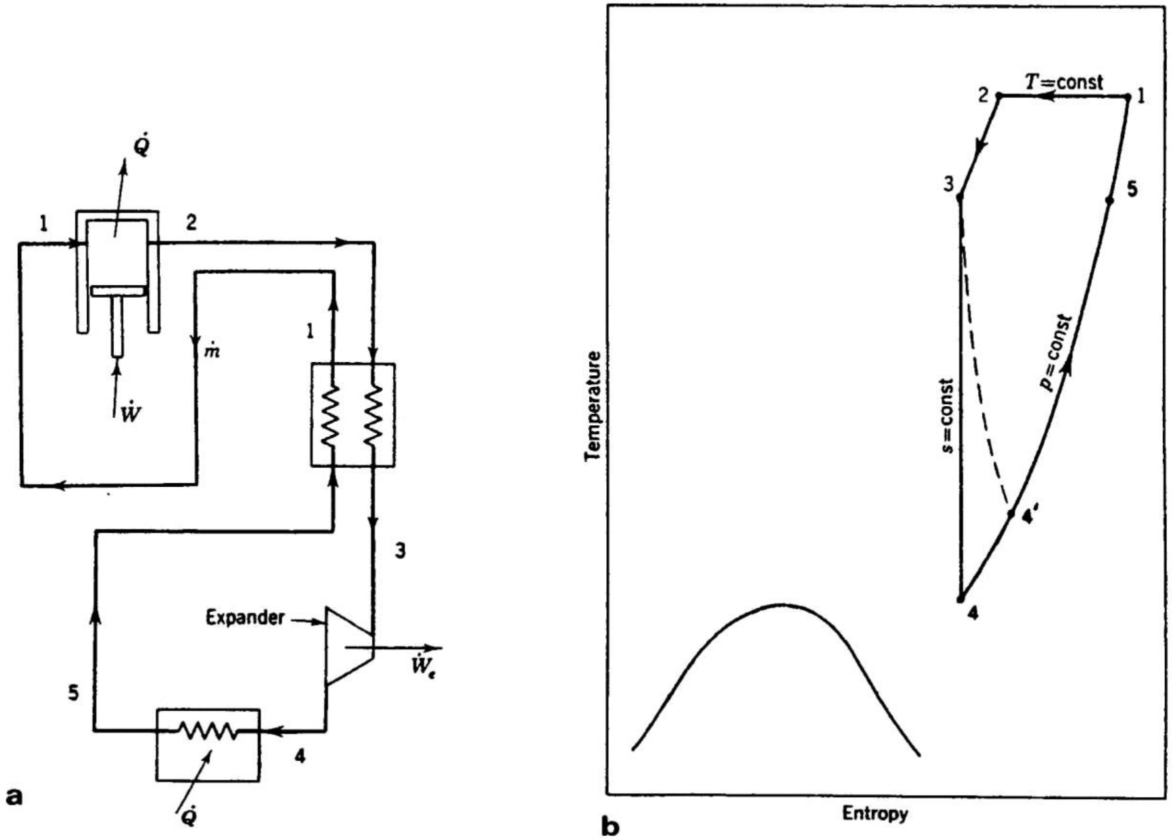
Turboexpander

- Linde turbine at right
- Expansion turbines are typically used in helium refrigerators larger than about 500 W.
- Real efficiencies (relative to isentropic) are 60% to 80%



A simplified real helium cycle

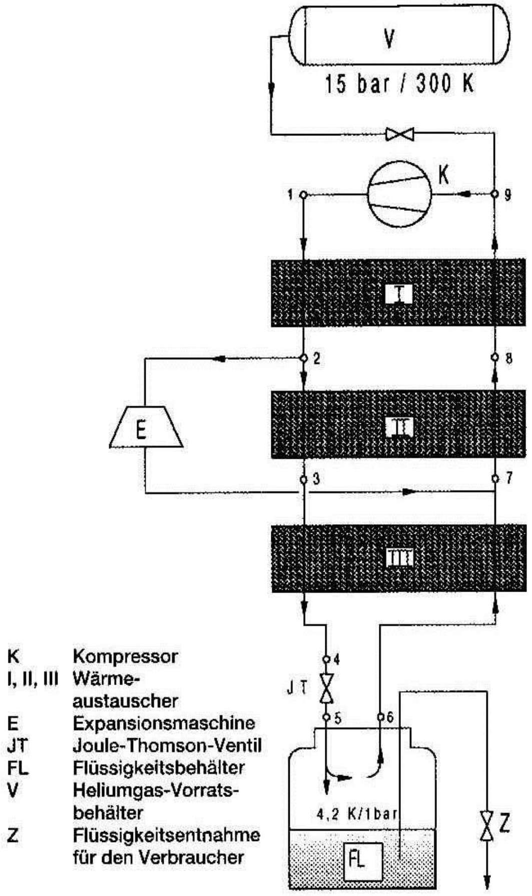
Klaus D. Timmerhaus and Thomas M. Flynn,
<u>Cryogenic Process Engineering</u>, p.126



A more typical modern helium cycle

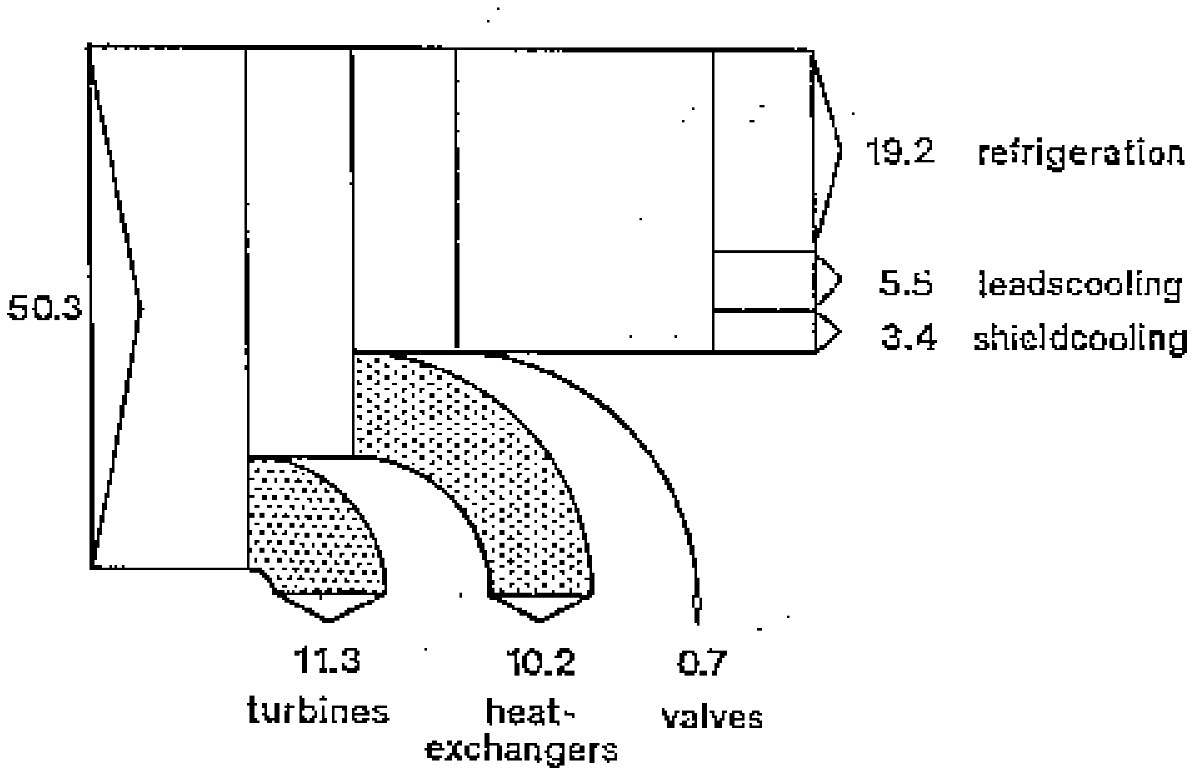
(but still simplified, from Linde Kryotechnik, AG)

- The “Claude process”, shown to the right, includes intermediate temperature expanders
- Modern cryoplants follow this pattern
- The HERA plants each have 7 turboexpanders



Cold box losses

from B. Ziegler, “Second Law Analysis of the Helium Refrigerators for the HERA Proton Magnet Ring,” in Advances in Cryogenic Engineering, Vol. 31, Plenum Press, 1986, p. 693



Helium cycle efficiency

	RHIC	CEBAF	HERA	LEP
Equivalent capacity at 4.5K (KW)	25	13	8.4 per coldbox	6 per coldbox
Power required in W/W	450	350	285	230
Efficiency	16%	20%	25%	30%

References

- Edward F. Obert, *Concepts of Thermodynamics*, McGraw-Hill, Inc., 1960.
- R. Byron Bird, Warren E. Stewart, Edwin N. Lightfoot, *Transport Phenomena*, John Wiley &Sons, 1960.
- S. W. VanSciver, *Helium Cryogenics*, Plenum Press, 1986.
- Mooney, David A., *Mechanical Engineering Thermodynamics*, Prentice-Hall, Inc., New York, 1953.

Question for discussion tomorrow

“Square wave engine”

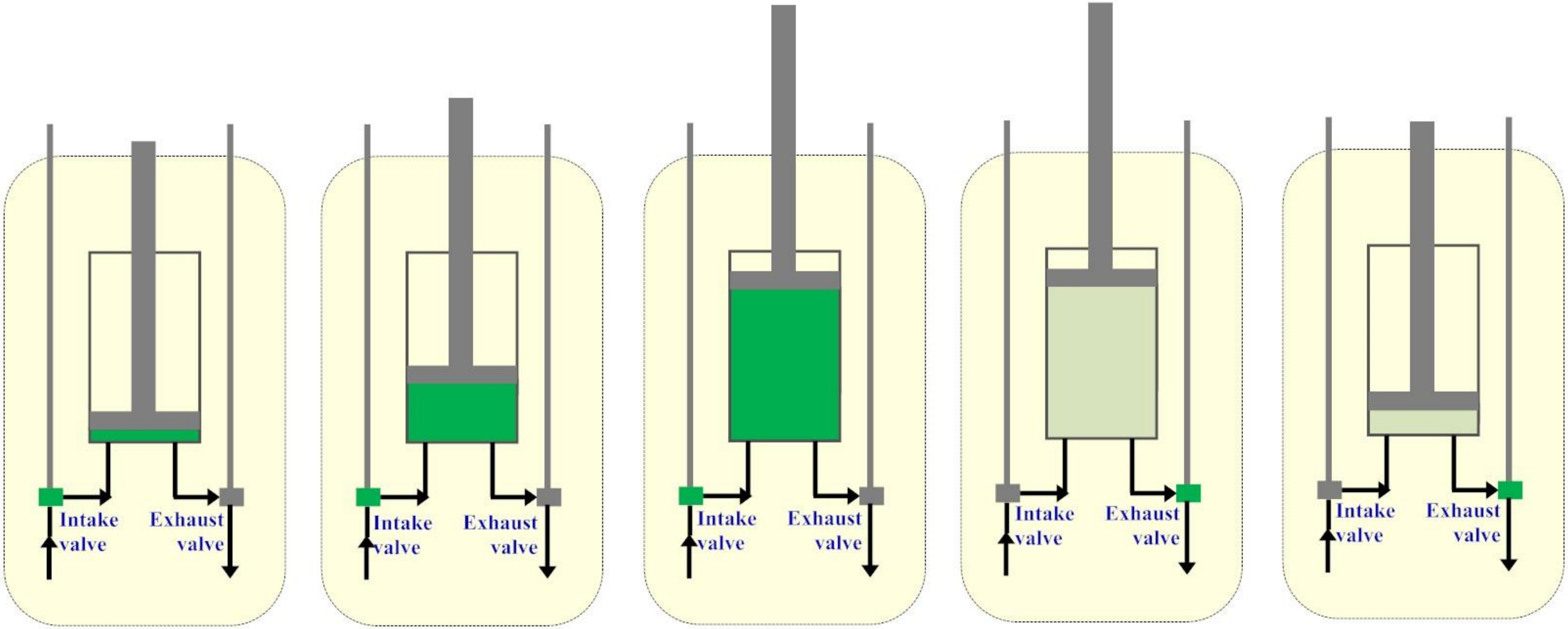
Square wave engine

illustrates an interesting thermodynamics problem

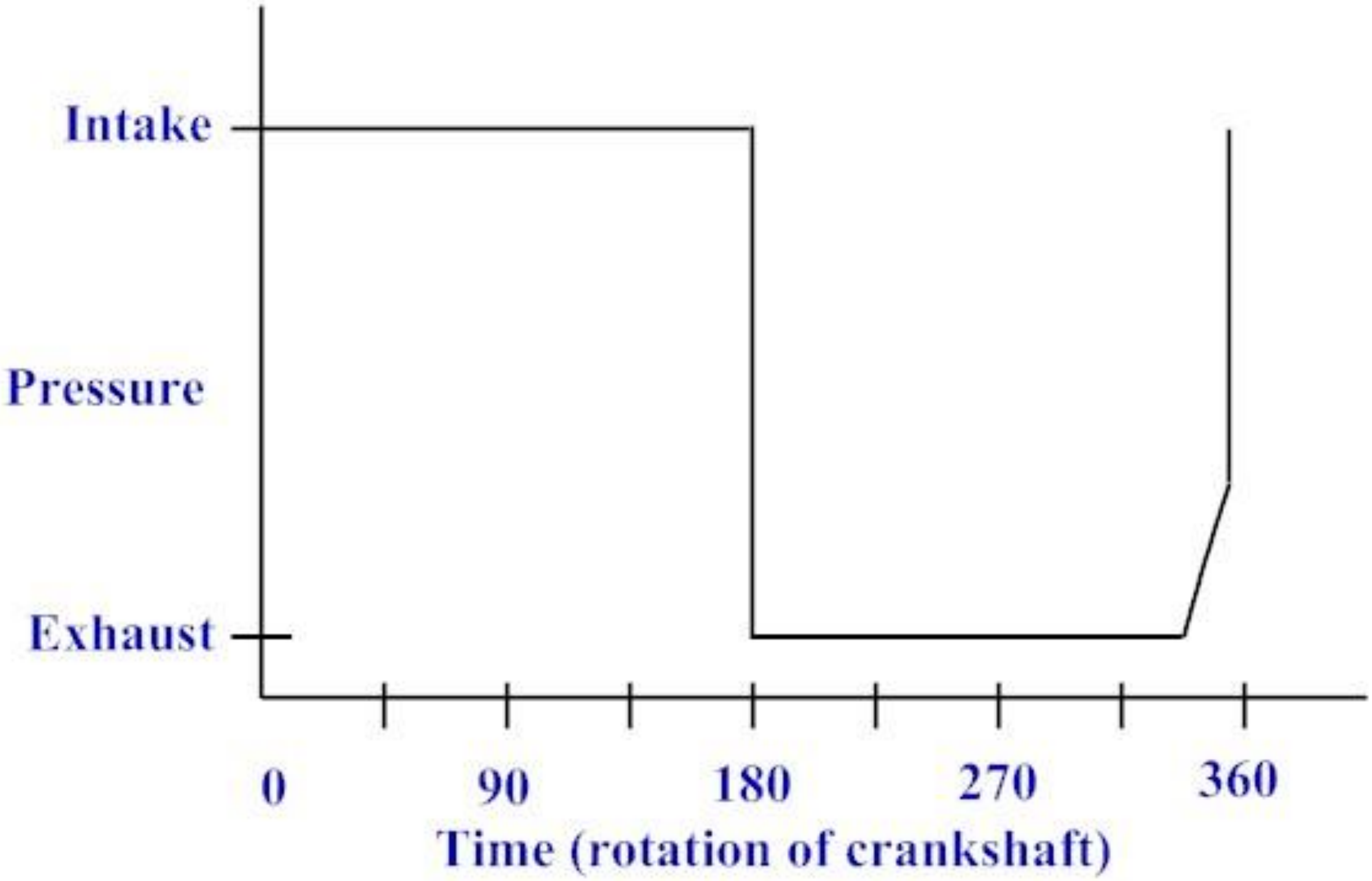
- "Square wave" engine problem
  - Suppose intake valve is open for entire 180 degree intake stroke
  - No closed-cylinder expansion
  - Intake valve closes, then exhaust valve opens, so cylinder contents blow down from intake pressure to discharge pressure

Intake valve open 180 degrees

Fill cylinder with intake valve open, then open exhaust valve



Square wave pressure trace



Square wave problem

- Entire intake stroke at higher pressure than entire discharge stroke
- Engine clearly does work, generates power
- But no isentropic expansion
  - No closed-cylinder expansion of any kind
- Where does power come from? What gas properties change, and how? We'll discuss that tomorrow.