Thermodynamics for Cryogenics

Ram C. Dhuley

USPAS – Cryogenic Engineering

June 21 – July 2, 2021

Goals of this lecture

- Revise important definitions in thermodynamics – system and surrounding, state properties, derived properties, processes
- Revise laws of thermodynamics and learn how to apply them to cryogenic systems
- Learn about 'ideal' thermodynamic processes and their application to cryogenic systems
- Prepare background for analyzing real-world helium liquefaction and refrigeration cycles.

🧬 **Fermilab**

Introduction

- Thermodynamics deals with the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy.

- Thermodynamics has its basis in attempts to understand combustion and steam power but is still "state of the art" in terms of practical engineering issues for cryogenics, especially in process efficiency.


James Dewar (invented vacuum flask in 1892)

https://physicstoday.scitation.org/doi/10.1063/1.881490

🔷 Fermilab

Definitions

- <u>Thermodynamic system</u> is the specified region in which heat, work, and mass transfer are being studied.
- <u>Surrounding</u> is everything else other than the system.
- <u>Thermodynamic boundary</u> is a surface separating the system from the surrounding.

🌠 Fermilab
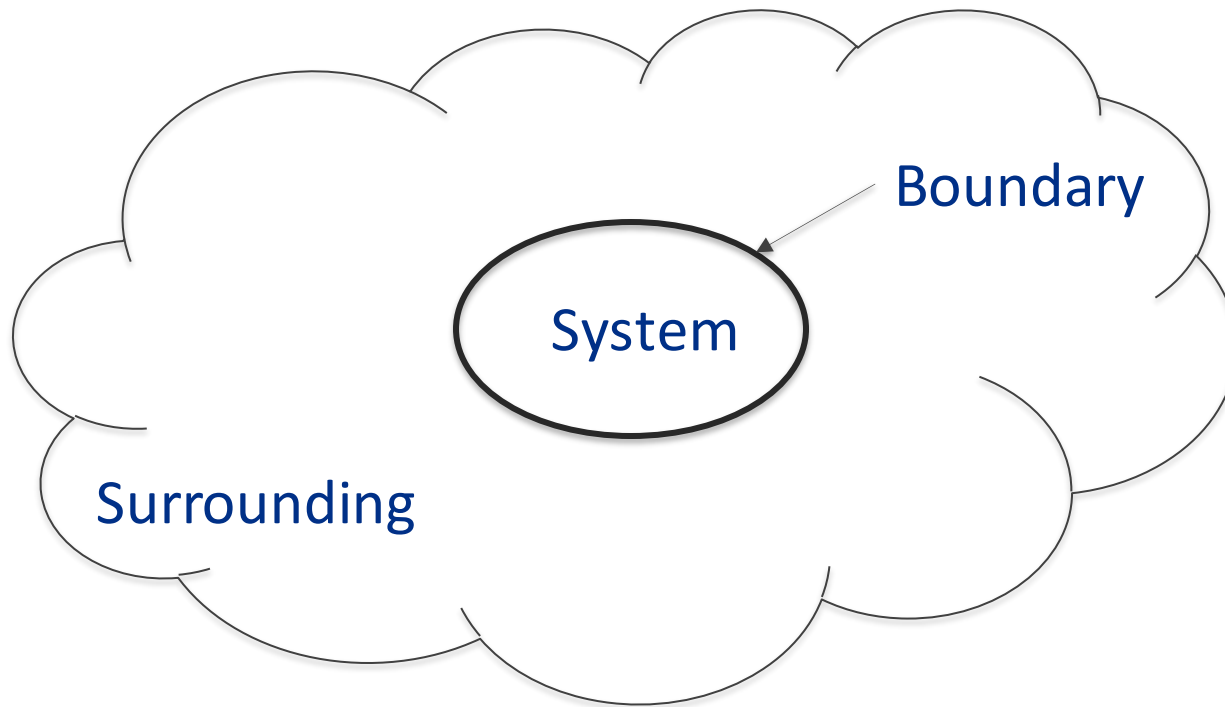
Definitions (continued)

Types of thermodynamic systems

- <u>Isolated system</u> has no exchange of mass or energy with its surrounding
- <u>Closed system</u> exchanges heat but not mass
- <u>Open system</u> exchanges both heat and mass with its surrounding

Thermodynamic State

- <u>Thermodynamic state</u> is the condition of the system at a given time, defined by 'state' properties
  - More details on next slides
- Two state properties define a state of a "homogenous" system
- Usually, three state properties are needed to define a state of a non-homogenous system (example: two phase, mixture)

🟦 **Fermilab**

Common state properties

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

‡ Fermilab

Common derived properties

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

$$c_v = \left. \frac{\partial u}{\partial T} \right|_v \qquad c_p = \left. \frac{\partial h}{\partial T} \right|_p$$

- 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

🔷 **Fermilab**

Thermodynamic Path and Process

Thermodynamic Path

- A path is series of intermediate states that a system takes while going from one (initial) state to another (final) state
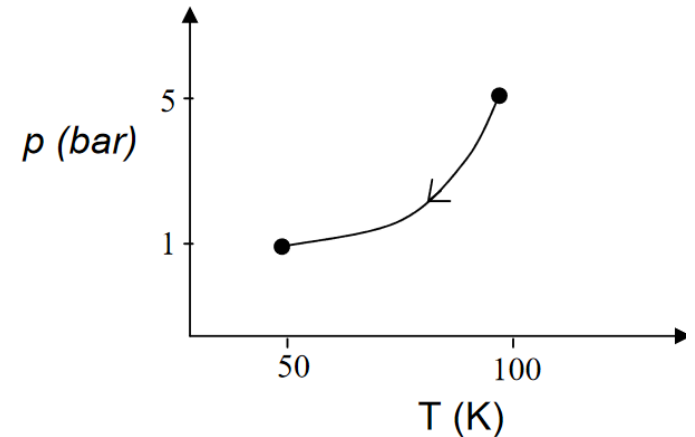
Thermodynamic Process

- <u>Process</u> defines the type of path taken by the system while going from initial to final state
  - Isothermal – constant temperature
  - Isobaric – constant pressure
  - Isochoric – constant volume
  - Isentropic – constant entropy
  - Isenthalpic – constant enthalpy

🟦 Fermilab

Equation of state

Equation of state (EOS) is a relation between the state parameters that a system obeys while changing from one state to another.

An example is **Ideal gas EOS**, given by $pv = RT$
where R is universal gas constant/gas molar mass
- good approximation for gases at low pressure and high temperature (far away from critical p and T)
- 'ideality' can be evaluated from <u>compressibility factor</u> Z = pv/RT (an ideal gas has Z = 1)

Several empirical EOS have been formulated for real gases, examples are **Van der Waals EOS, Peng Robinson EOS**

🟦 **Fermilab**

Compressibility factor for helium
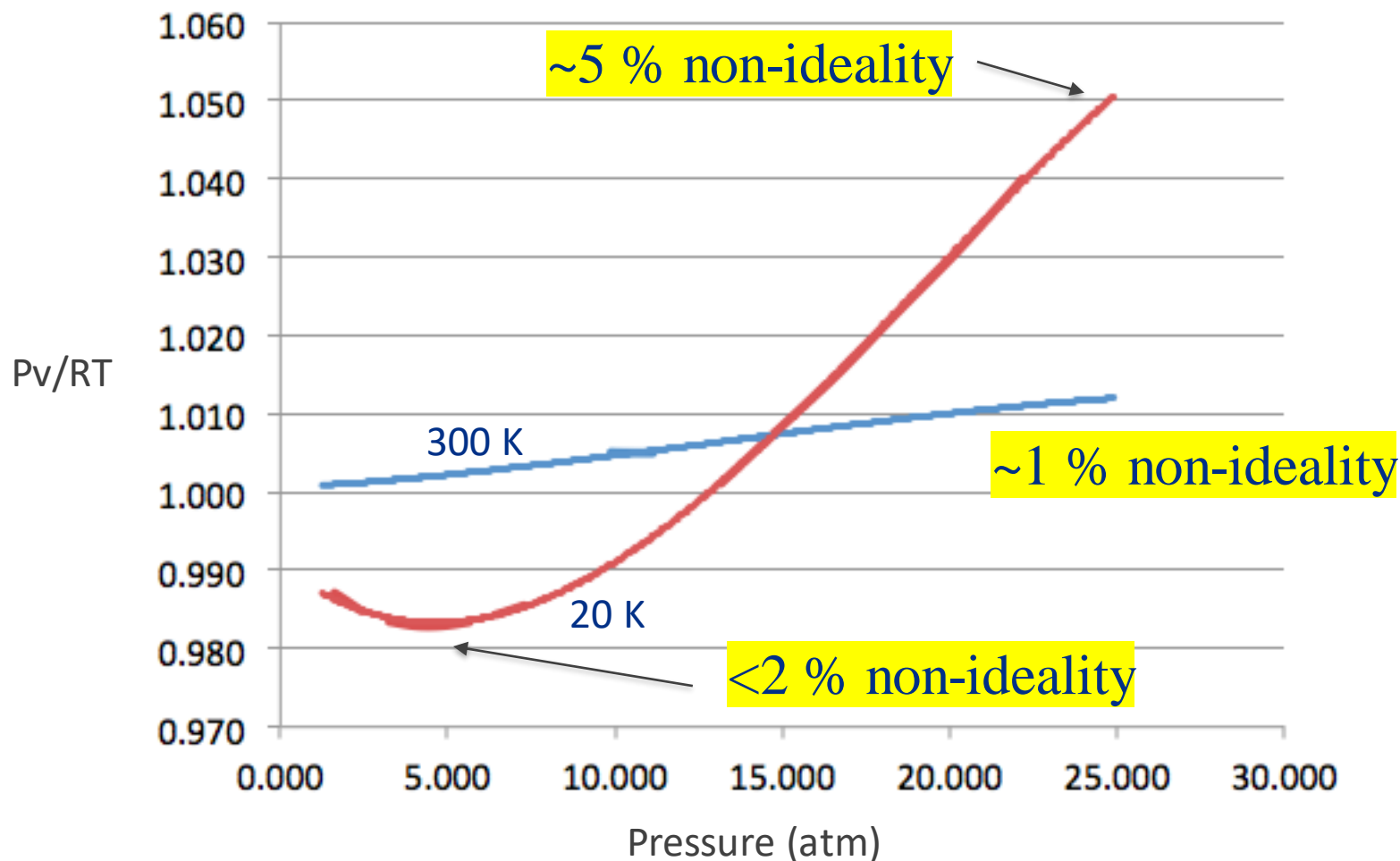
Helium has <10% non-ideality down to 8 K

🟦 Fermilab

More about ideal gases

- The internal energy of an ideal gas is a function of temperature alone, $Du = c_v DT$ where c_v is constant

- Since h = u +Pv, so h = u + RT for an ideal gas, enthalpy is also a function of temperature alone for an ideal gas, $Dh = c_p DT$ where c_p is constant.
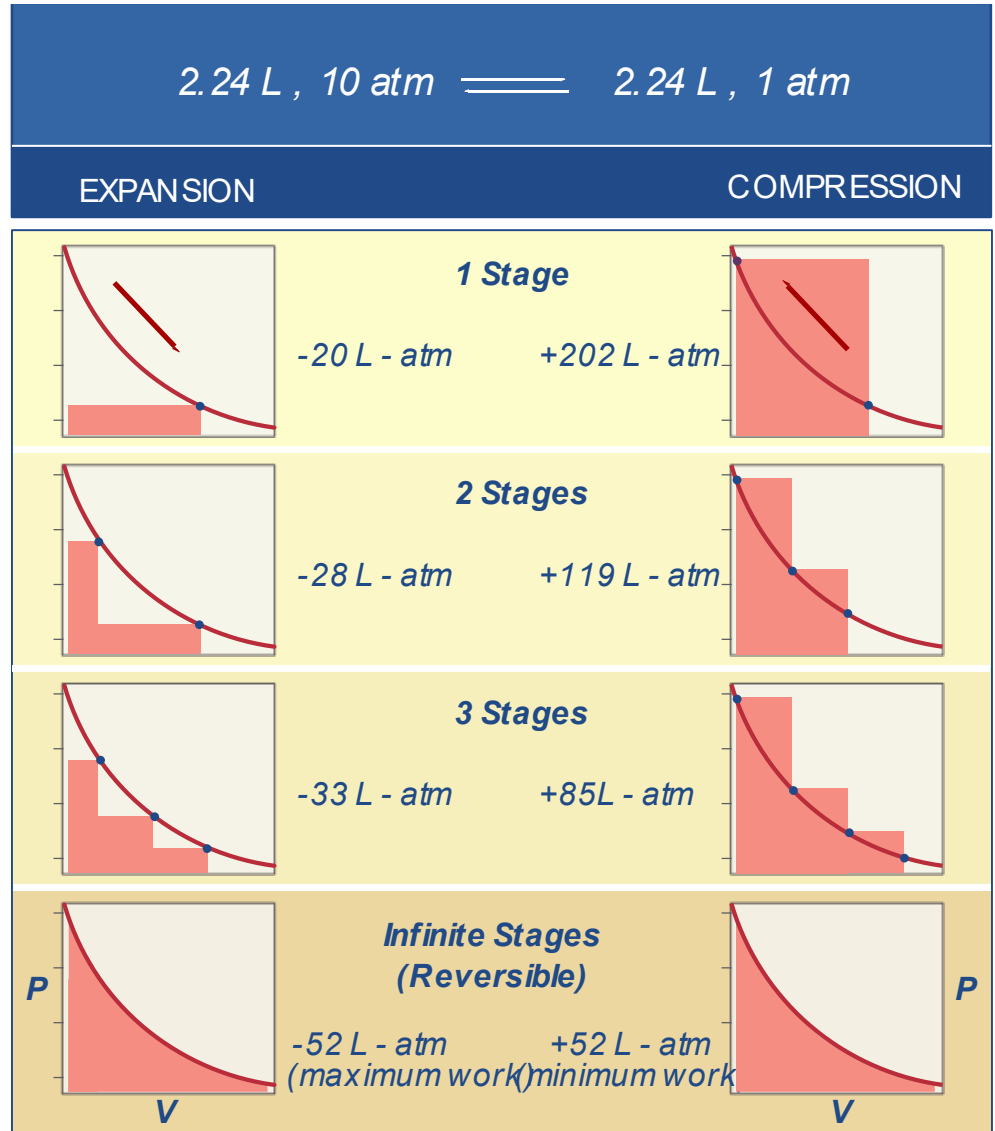
🎇 **Fermilab**

Reversible process

A *theoretical* process in which state of a system is changed in a series of *infinitesimal steps* such that at every step the system holds equilibrium with its surrounding. At every step, the change can be "undone" to restore the system to its prior state.

In the context of refrigeration/cryogenics, a reversible process
- consumes the least amount of mechanical power (work) for compression
- produces maximum mechanical power (work) during expansion

🎇 **Fermilab**

Reversible process

Process done in large, discreet steps (irreversible)

Process done infinitesimal steps (reversible)

2.24 L , 10 atm ===== 2.24 L , 1 atm

EXPANSION | COMPRESSION

1 Stage
-20 L - atm   +202 L - atm

2 Stages
-28 L - atm   +119 L - atm

3 Stages
-33 L - atm   +85L - atm

Infinite Stages (Reversible)
-52 L - atm   +52 L - atm
(maximum work) (minimum work)

P   V   V   P

Ram C. Dhuley | USPAS Cryogenic Engineering (Jun 21 - Jul 2, 2021)

🎇 Fermilab

The laws of thermodynamics

- **Zeroth law** – Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other

- **First law** – The total energy of a system is conserved during a thermodynamic process

- **Second law** – The entropy of a system increases in all real processes and is conserved in reversible processes

- **Third law** – The entropy of a pure substance in complete thermodynamic equilibrium becomes zero at a temperature of absolute zero

🐝 **Fermilab**

The laws of thermodynamics
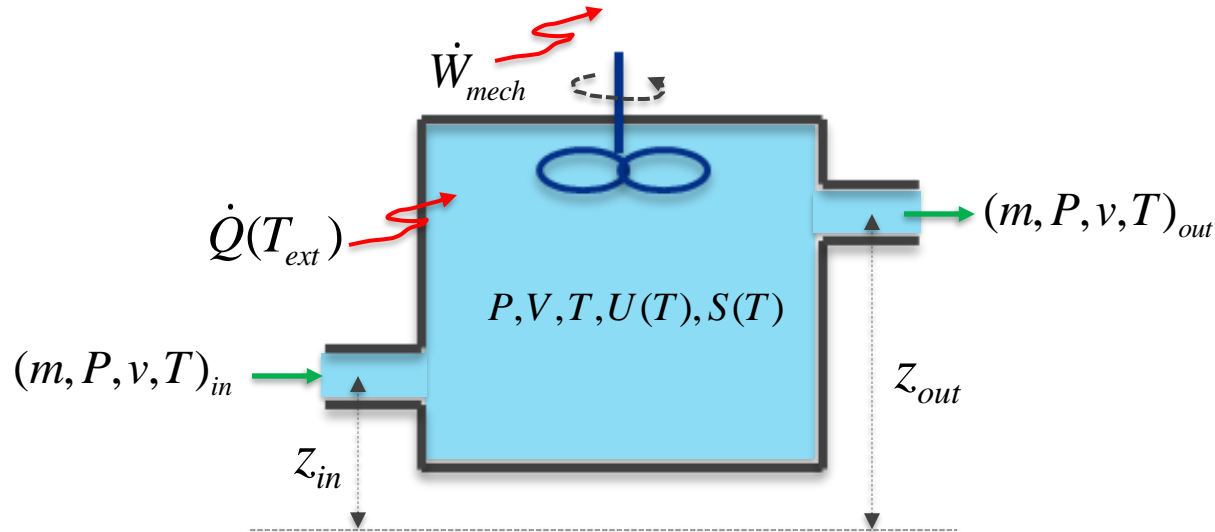
First law:
$$\frac{dU}{dt} = \sum \dot{Q} - \sum \dot{W}_{mech} + \sum_{in} \dot{m}\left(h + \frac{v^2}{2} + gz\right) - \sum_{out} \dot{m}\left(h + \frac{v^2}{2} + gz\right)$$

Second law:
$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T_{ext}} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s + \dot{S}_{gen} \quad \text{with} \quad \dot{S}_{gen} \geq 0$$

Notes:
- Time derivative terms are zero for steady state processes
- Mass flow terms are zero for closed systems
- Sign convention: Inward = positive, outward = negative

🟦 **Fermilab**

Isothermal compression

Reversible, constant temperature compression - requires the least amount of mechanical work to pressurize a fluid

- Sets an upper limit on the efficiency of compression, aka 'isothermal efficiency'

Isothermal compressor
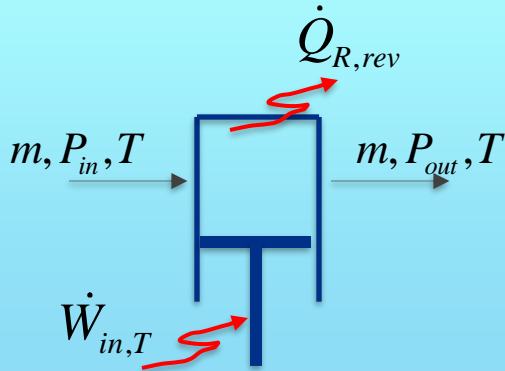
Let's apply laws of thermodynamics to determine work of isothermal compression at <u>steady state</u>

- Neglect changes in kinetic and potential energy
- Assume ideal gas, $Pv = RT$

First law: $\dfrac{dU}{dt} = 0 = -\dot{Q}_{R,rev} + \dot{W}_{in,T} + \dot{m}\underline{(h_{in} - h_{out})}$

=0 for ideal gas

Second law: $\dfrac{dS}{dt} = 0 = \dfrac{-\dot{Q}_{R,rev}}{T} + \dot{m}(s_{in} - s_{out}) + \underline{\dot{S}_{gen}}$

=0 for a reversible process

Combine, re-arrange, and use ideal gas EOS:

$$\dot{W}_{in,T} = \dot{Q}_{R,rev} = \dot{m}(s_{in} - s_{out})T$$
$$= \dot{m}RT \ln(p_{out} / p_{in})$$

🟦 **Fermilab**

Isothermal compression

An example from Fermilab

- 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 is

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

- 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

🐟 Fermilab
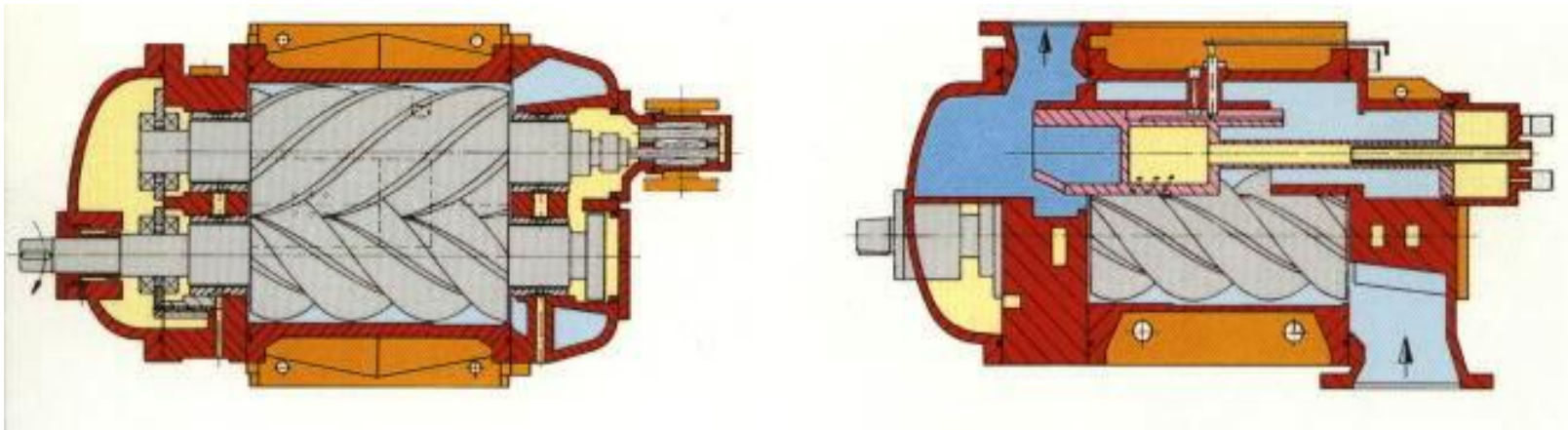
Isentropic expansion

Reversible expansion of a fluid without exchange of heat

- The expansion produces mechanical work at the expense of enthalpy loss, which results in cooling
- Produces maximum change in enthalpy and sets an upper limit on the efficiency of cooling via expansion, aka 'isentropic efficiency'

Isentropic expander

m, P_{in}, T_{in}

$\dot{W}_{out,s}$

m, P_{out}, T_{out}
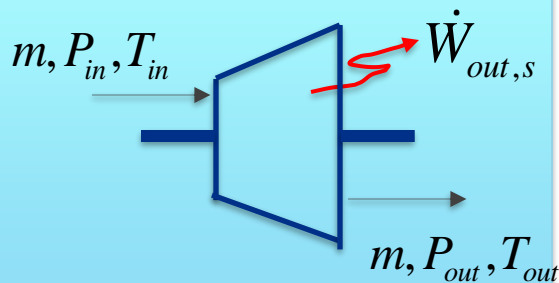
Let's apply laws of thermodynamics to determine work of isentropic expansion at steady state

- Neglect changes in kinetic and potential energy
- Assume ideal gas, Pv = RT

First law: $\dfrac{dU}{dt} = 0 = \dot{Q} - \dot{W}_{out,s} + \dot{m}(h_{in} - h_{out})$

=0 for isentropic process

Second law: each term is identically zero

Rearrange first law and use ideal gas EOS:

$$\dot{W}_{out,s} = \dot{m}(h_{in} - h_{out}) = \dot{m}c_p(T_1 - T_2)$$

🔷 Fermilab

Isentropic expansion

Isentropic efficiency

- Isentropic expansion efficiency is defined as

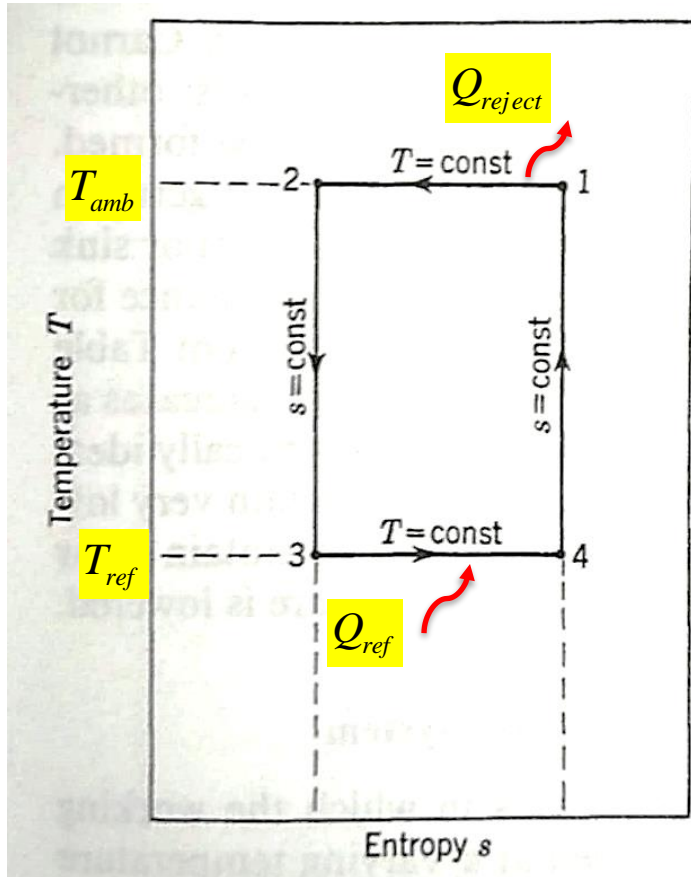$$\frac{\mathrm{D}h_{real}}{\mathrm{D}h_{isentropc}}$$

  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%

🔀 **Fermilab**

Thermodynamically ideal refrigerator

Type 1: Refrigeration load is isothermal (constant T)

- The medium to be cooled is at constant temperature

Processes:

- 1 -> 2 – isothermal compression
- 2 -> 3 – isentropic expansion
- 3 -> 4 – isothermal heat absorption (ref. load)
- 4 -> 1 – isentropic compression

Apply first law to the entire cycle:

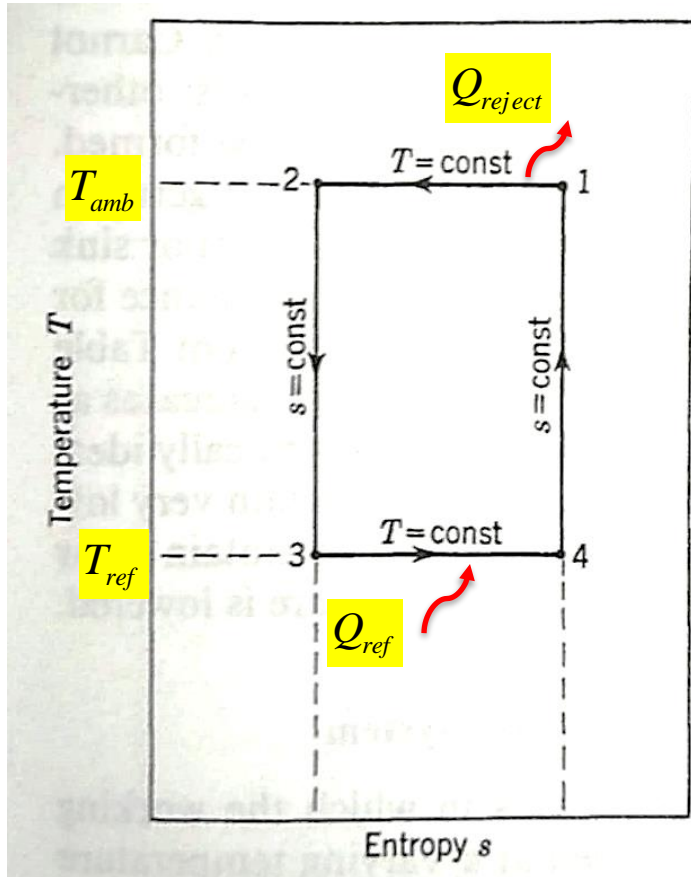Cyclic process: $\Delta u = 0 = Q_{net} - \dot{W}_{net,in}$

Net work input:

$$\dot{W}_{net,in} = T_{amb}(s_2 - s_1) - T_{ref}(s_4 - s_3)$$

$$= (T_{amb} - T_{ref})(s_4 - s_3) = Q_{net}$$

Refrigeration power: $Q_{ref} = T_{ref}(s_4 - s_3)$

🎇 Fermilab

Thermodynamically ideal refrigerator

Type 1: Refrigeration load is isothermal (constant T)

- The medium to be cooled is at constant temperature

Coefficient of performance (COP):

- Defined as the ratio of refrigeration load to net input mechanical work (*i.e.*, benefit/cost)

$$COP_{isoT,ideal} = \frac{Q_{ref}}{\dot{W}_{net,in}} = \frac{T_{ref}}{T_{amb} - T_{ref}}$$

The COP of an ideal gas, ideal isothermal load refrigerator:

- depends only on ambient and load temperatures
- does not depend on the fluid or its pressure
- represents the highest refrigeration power one can get for a given work input

Eg: $COP_{isoT,ideal} = 0.013$ for $T_{ref} = 4\,K$ and $T_{amb} = 300\,K$

At least 77 W (=1/0.013) of mechanical power input is needed at 300 K to obtain 1 W refrigeration at 4 K

🔹 Fermilab

Thermodynamically ideal refrigerator

Type 2: Refrigeration load is non-isothermal

- Temperature of the medium increases as refrigeration load is absorbed
- Typically, the pressure remains constant (isobaric ref. load)
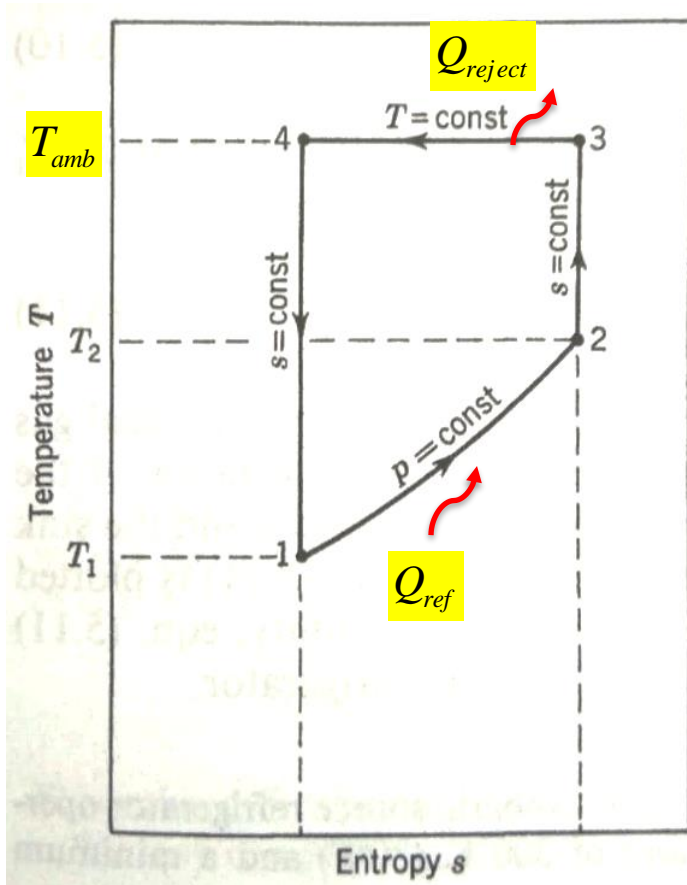
Processes:

- 1 -> 2 – isobaric heat absorption (ref. load)
- 2 -> 3 – isentropic compression
- 3 -> 4 – isothermal compression
- 4 -> 1 – isentropic expansion

Apply first law to the entire cycle:

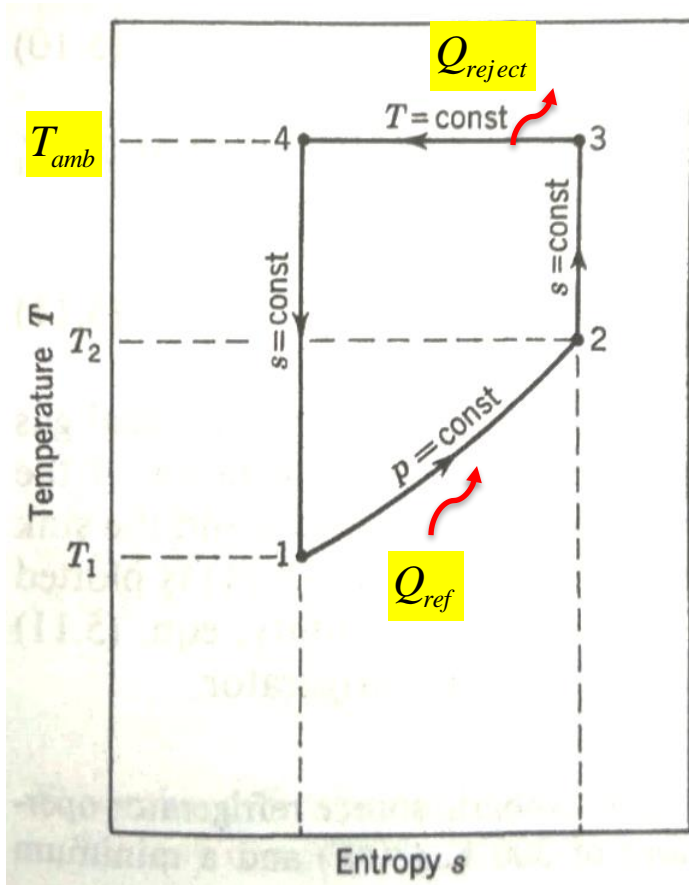Cyclic process: $\Delta u = 0 = Q_{net} - \dot{W}_{net,in}$

Net work input:

$$\dot{W}_{net,in} = Q_{net} = Q_{reject} - Q_{ref}$$
$$= T_{amb}(s_4 - s_3) - Q_{ref}$$
$$= T_{amb}(s_2 - s_1) - Q_{ref}$$

Thermodynamically ideal refrigerator

Type 2: Refrigeration load is non-isothermal

- Temperature of the medium increases as refrigeration load is absorbed
- Typically, the pressure remains constant (isobaric ref. load)

Apply first law to the entire cycle:

Refrigeration power:

$$Q_{ref} = \int_1^2 Tds = \int_1^2 (dh - vdP) = h_2 - h_1$$

Coefficient of performance (COP):

$$COP_{isoP,ideal} = \frac{Q_{ref}}{\dot{W}_{net,in}} = \frac{h_2 - h_1}{T_{amb}(s_2 - s_1) - (h_2 - h_1)}$$

If the fluid is an ideal gas,

$$COP_{isoP,ideal} = \frac{(T_2/T_1) - 1}{(T_{amb}/T_1)\ln(T_2/T_1) - ((T_2/T_1) - 1)}$$

🟦 Fermilab

Isenthalpic expansion

A simple, commonly used method to produce cooling

- 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

$$\left(\frac{\partial T}{\partial P}\right)_h = 0 \quad \text{For ideal gases}$$

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

🌠 **Fermilab**

Isenthalpic expansion

Joule Thompson expansion

- In real fluids, including helium, isenthalpic expansion may provide temperature drop
  - Starting P and T need to be on the 'left' side of inversion curve where $(dP/dT)|_h > 0$

- Joule-Thomson expansion through a valve is said to be through a "J-T valve"
  - Not as efficient of isentropic expansion
  - But very convenient and easy (no moving parts)
  - Used frequently as the final expansion stage in real helium refrigerators, liquefiers

$$\frac{dP}{dT}\bigg|_h < 0$$

$$\frac{dP}{dT}\bigg|_h > 0$$
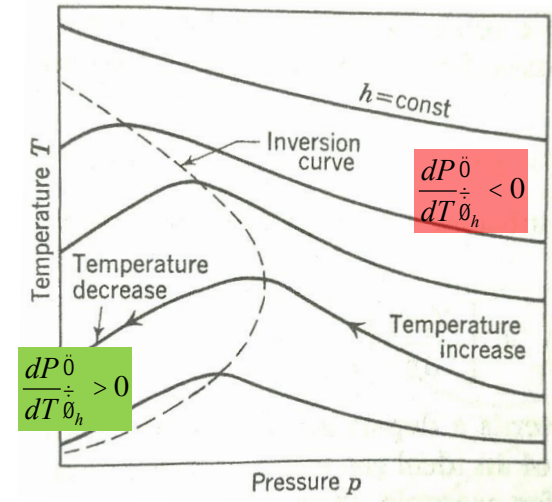
Gas	Maximum Inversion Temperature	
	K	°R
Helium-4	45	81
Hydrogen	205	369
Neon	250	450
Nitrogen	621	1118
Air	603	1085
Carbon monoxide	652	1174
Argon	794	1429
Oxygen	761	1370
Methane	939	1690
Carbon dioxide	1500	2700
Ammonia	1994	3590

🎲 Fermilab

Source of state properties for thermodynamic analyses

Temperature entropy chart for helium

🟰 Fermilab
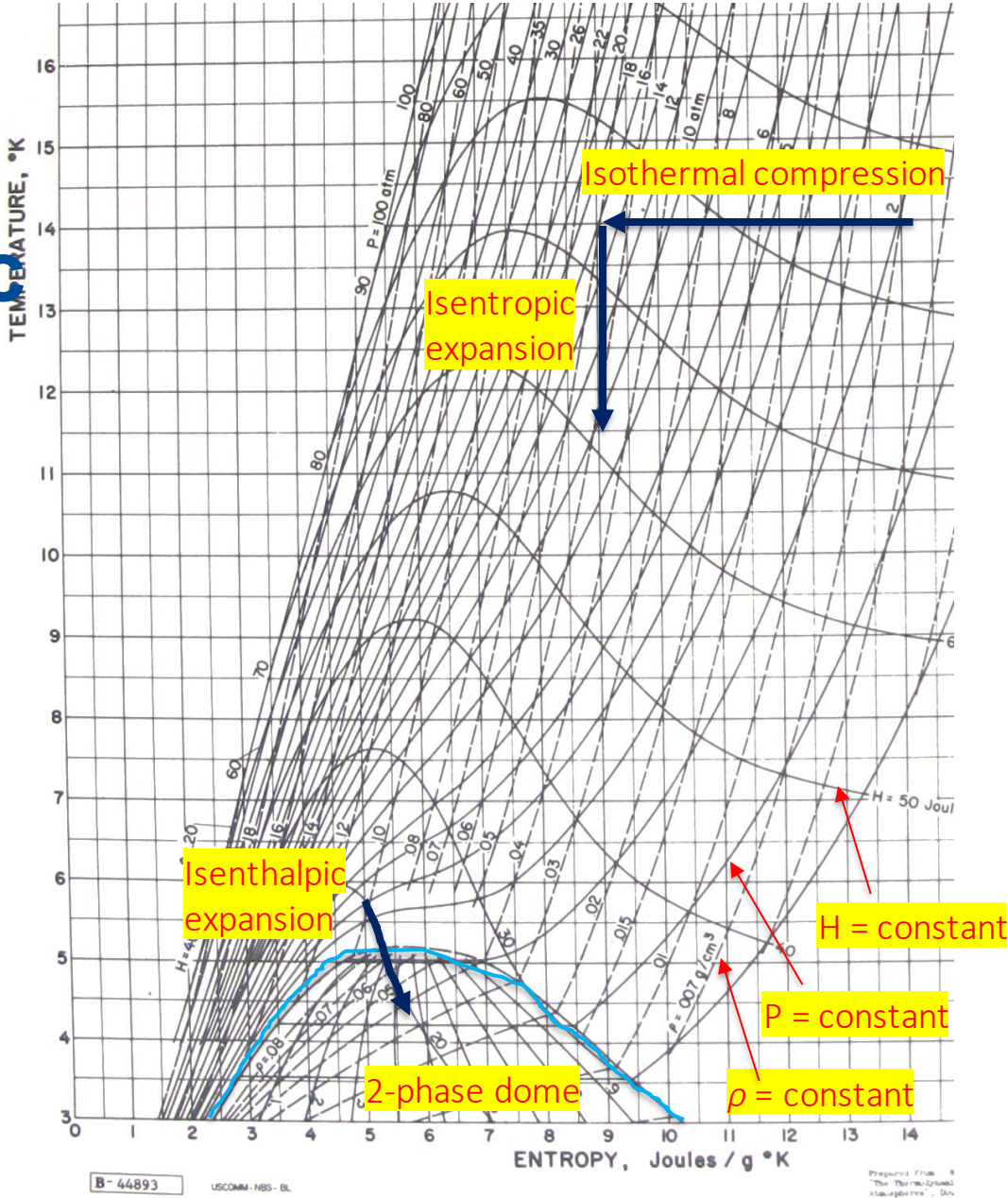
Source of state properties for thermodynamic analyses

NIST Thermophysical Properties of Fluid Systems
(https://webbook.nist.gov/chemistry/fluid/)

Thermophysical Properties of Fluid Systems

Accurate thermophysical properties are available for several fluids. These data include the following:

- Density
- C_p
- Enthalpy
- Internal energy
- Viscosity
- Joule-Thomson coefficient

- Specific volume
- C_v
- Entropy
- Speed of Sound
- Thermal conductivity
- Surface tension (saturation curve only)

🎇 **Fermilab**

How to use the NIST webbook?

1. Please select the species of interest:

   Helium ▾

2. Please choose the units you wish to use:

   Temperature

   ⦿ Kelvin   ○ Celsius   ○ Fahrenheit   ○ Rankine

   Pressure

3. Choose the desired type of data:

   Data type

   ⦿ Isothermal properties
   ○ Isobaric properties
   ○ Isochoric properties
   ○ Saturation properties — temperature increments
   ○ Saturation properties — pressure increments

4. Please select the desired standard state convention:

   Standard state convention

   ⦿ Default for fluid
   ○ Normal B.P. convention
   ○ ASHRAE convention
   ○ IIR convention

5. **Press to Continue**

🔷 Fermilab

How to use the NIST webbook?

1. Enter temperature in selected units:

   `300` (Acceptable range: 2.1768 to 1500.0 K)

2. Enter pressure range and increment in selected units:

   P_{Low} `1`   (min value: 0.0 bar)

   P_{High}*   `20`

   $P_{Increment}$ `1`

- Fluid Data
- Auxiliary Data
- References
- Additional Information
- Important Information About This Data
- Notes
- **Other Data Available:**
  - View data in HTML table.
  - Download data as a tab-delimited text file.

🎇 **Fermilab**

How to use the NIST webbook?

Isothermal Data for T = 300.00 K

Temperature (K)	Pressure (bar)	Density (kg/m3)	Volume (m3/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (K/bar)	Viscosity (Pa*s)	Therm. Cond. (W/m*K)	Phase
300.00	1.0000	0.16040	6.2345	940.00	1563.5	28.027	3.1160	5.1930	1019.6	-0.062201	1.9930e-05	0.15597	vapor
300.00	2.0000	0.32065	3.1187	940.04	1563.8	26.587	3.1162	5.1929	1020.0	-0.062203	1.9933e-05	0.15605	vapor
300.00	3.0000	0.48075	2.0801	940.08	1564.1	25.745	3.1164	5.1928	1020.4	-0.062205	1.9937e-05	0.15613	vapor
300.00	3.0000	0.48075	2.0801	940.08	1564.1	25.745	3.1164	5.1928	1020.4	-0.062205	1.9937e-05	0.15613	supercritical
300.00	3.0000	0.48075	2.0801	940.08	1564.1	25.745	3.1164	5.1928	1020.4	-0.062205	1.9937e-05	0.15613	supercritical

Data from this table can be copied to a spreadsheet or exported as a tab-delimited file.

🔷 **Fermilab**

References

1. R. Barron, "Cryogenic Systems", Oxford University Press; 2nd edition (June 13, 1985).

2. NIST database: Thermophysical Properties of Fluid Systems, https://webbook.nist.gov/chemistry/fluid/.

3. A nice explanation of reversible processes - https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Principles_of_Modern_Chemistry_(Oxtoby_et_al.)/Unit_4%3A_Equilibrium_in_Chemical_Reactions/13%3A_Spontaneous_Processes_and_Thermodynamic_Equilibrium/13.4%3A_Entropy_Changes_in_Reversible_Processes

Fermilab