Lecture 2
Properties Of Cryogenic Fluids

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Goals

- Introduce basic definitions used in describing cryogenic fluids & their properties
- Describe important fluid properties and their variation with temperature and pressure
- Introduce the law of corresponding states
- Describe where fluid properties may be found
- Mention unique properties of Hydrogen & Helium (more in later lectures)

Introduction

- Due to the wide temperature & pressure ranges covered by cryogenics the properties of fluids vary greatly – we generally can't assume constant properties.
- Understanding changes in the thermodynamic state of the fluids allows us to describe refrigeration and liquefaction cycles
- With the exception of Helium and Hydrogen, pure cryogenic fluids act as classical Newtonian fluids
- Fluid properties are well known (mostly) & many resources exist

Typical Properties

- Density
- Specific Heat
- Enthalpy (h (J / kg)): $h = u + Pv$
- Entropy (s (J / Kg K)): In a reversible process: $ds = dQ/T$
- Thermal Conductivity
- Viscosity

Some Definitions

- Supercritical Fluid: a fluid that may no longer be thought of as a liquid or a gas but only as a fluid. Such a fluid is either above its critical temperature or critical pressure or both.
  - The accuracy of calculated thermodynamic values becomes relatively inaccurate around the critical point
- Subcooled or Pressurized Liquid: A liquid whose temperature or pressure places it below the saturation curve
- Triple Point: The point in thermodynamic space in which the solid, liquid and vapor phases of a substance coexist.
- T-S (temperature – entropy) Diagram: Used to both display graphically fluid properties and frequently to describe refrigeration cycles
- Isenthalpic Expansion: changing from high to low pressure along a line of constant enthalpy

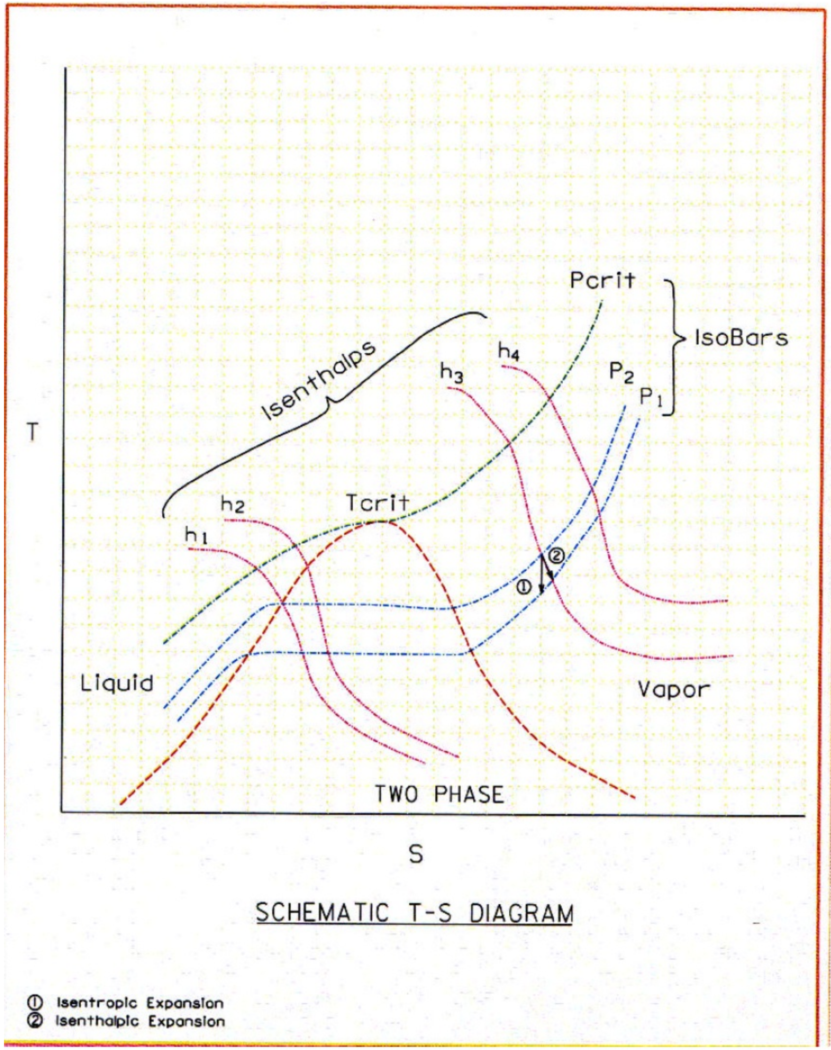
Some Definitions

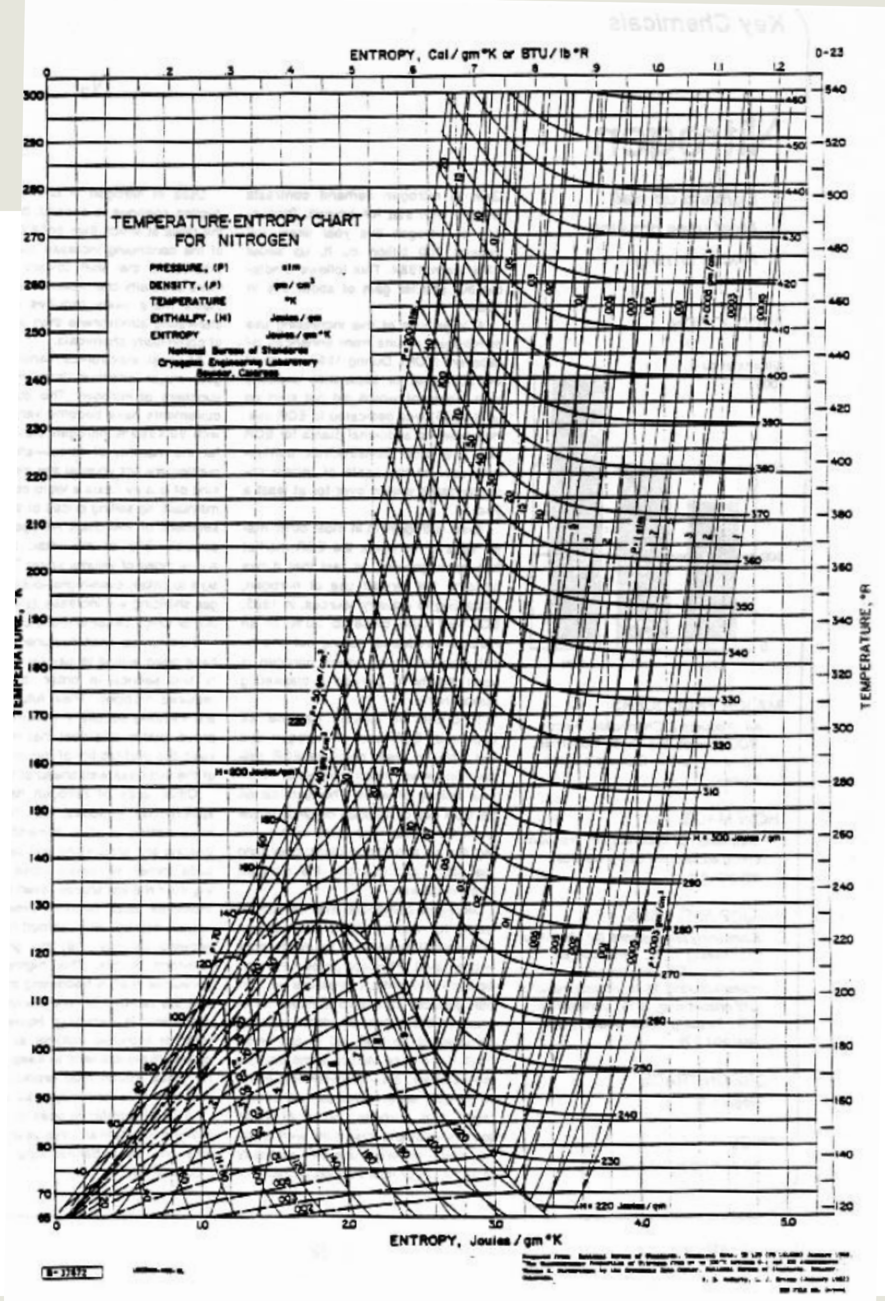
- <u>Isentropic Expansion:</u> changing from high to low pressure along a line of constant entropy
- <u>1st Order Phase Transition:</u> A change in phase in which there is a discontinuity in the specific heat and which requires latent heat
- <u>2nd Order Phase Transition:</u> No discontinuity in specific heat and no latent heat is required

Some Key Parameters of Cryogenic Fluids

Fluid	Normal Boiling Point (K)	Triple Point (K)	Critical Temperature (K)	Critical Pressure (kPa)
Krypton	119.8	115.8	209.4	5496
Methane	111.6	90.7	190.6	4599
Oxygen	90.2	54.4	154.6	5043
Argon	87.3	83.8	150.9	4906
Nitrogen	77.4	63.2	126.3	3399
Neon	27.1	24.6	44.4	2703
Hydrogen	20.3	13.8	32.9	1283.8
Helium	4.2	N/A	5.2	227.46

Generic T-S diagram Showing Isenthalps, Isobars and 2 Phase Region



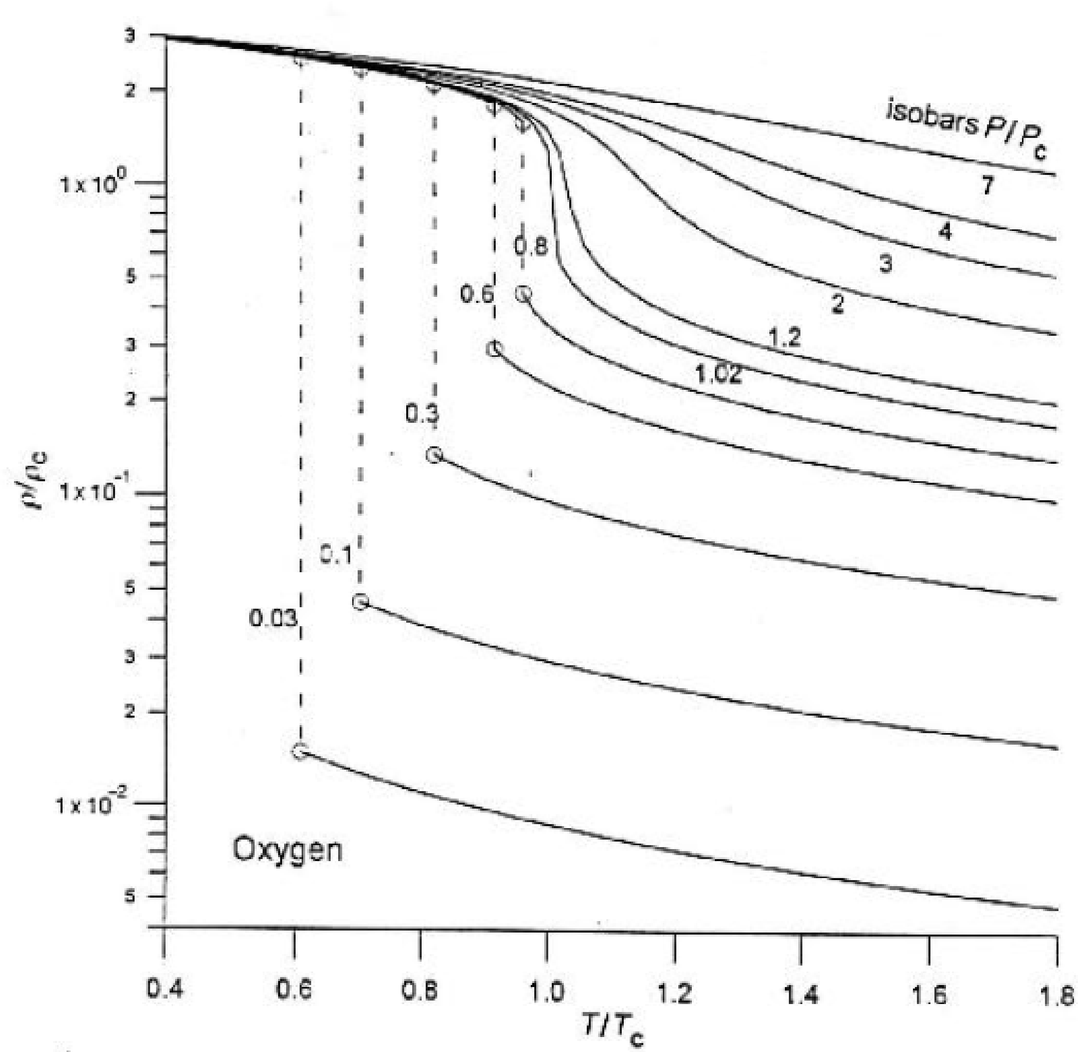


ENTROPY, Cal / gm °K or BTU / lb °R
TEMPERATURE-ENTROPY CHART
FOR NITROGEN
PRESSURE, (P) atm
DENSITY, (ρ) gm / cm³
TEMPERATURE °K
ENTHALPY, (H) Joules / gm
ENTROPY Joules / gm °K
TEMPERATURE, °K
TEMPERATURE, °R
H = 200 Joules / gm
H = 300 Joules / gm
H = 220 Joules / gm
ENTROPY, Joules / gm °K

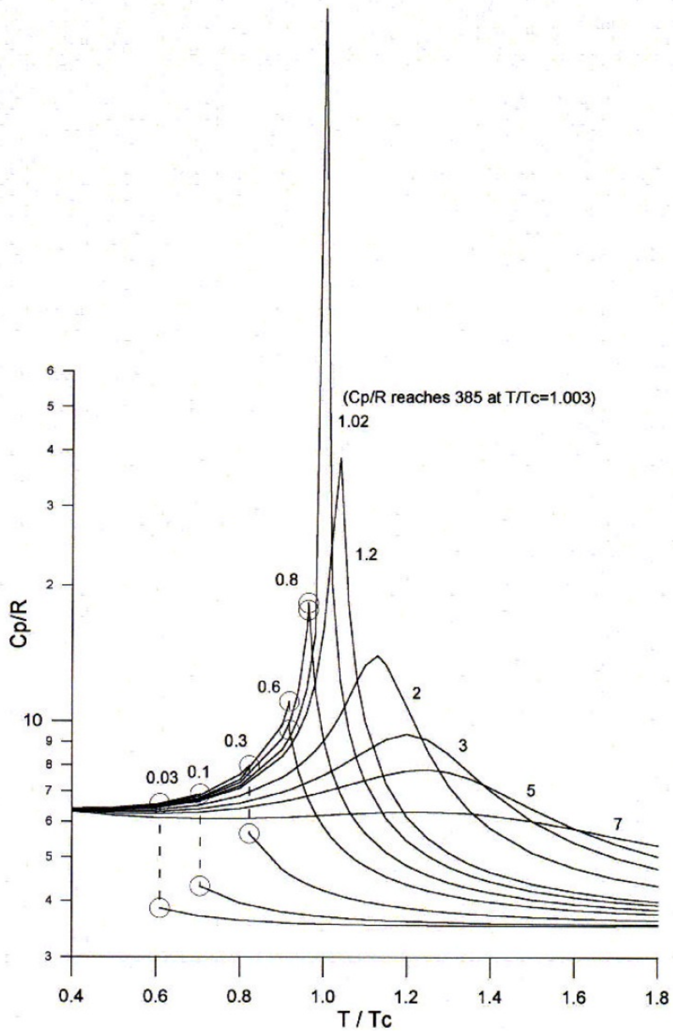
The Law of Corresponding States

- With the exception of helium and hydrogen, the properties of cryogenic fluids can be scaled from one fluid to another with a fair accuracy provided the properties have been normalized (typically by the critical properties of the fluid).
- This is useful in looking at the general shape of properties

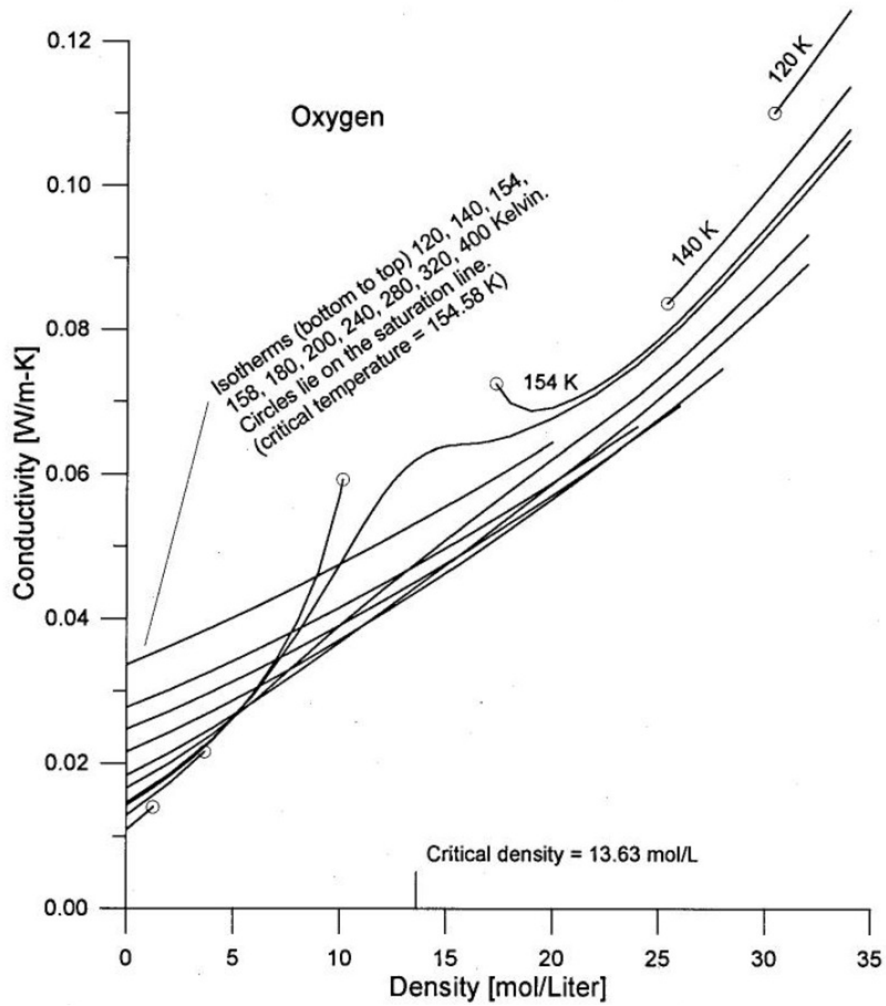
Normalized Density of Oxygen as a Function of Pressure &Temperature



Cp/R for Oxygen as a Function of Pressure & Temperature



Thermal Conductivity of Oxygen



Equations of State

- Allow calculation of all thermodynamic state properties
- In theory, are based on the interactions of a molecule with its neighbors
- In reality, are highly empirical
  - A simple example is the ideal gas law: $A(\rho,T) = RT\,(\log \rho - a \log T + S_0)$
- a = 3/2 for a monatomic gas, 5/2 for a diatomic etc.
- Best calculated via computer codes

Fluid Property Computer Codes

- The use of computer codes to generate properties (based typically on equations of states and empirical data) is the most common way to find fluid properties today
- Examples include:
  - NIST – 12 National Institute for Standards & Technology http://www.nist.gov/srd/nist23.cfm
  - GASPAK & HEPAK from CryoData http://www.htess.com/software.htm
  - An interactive website also from NIST should suffice for this class http://webbook.nist.gov/chemistry/fluid/

Additional Sources for Cryogenic Fluids Data

- "A Reference Guide for Cryogenic Properties of Materials", Weisend, Flynn, Thompson; SLAC-TN-03-023 (on Indico page)
  - This is a detailed bibliography for cryogenics material properties and includes fluids
- Thermodynamic Properties of Cryogenic Fluids, R. Jacobson et al.,
- Cryogenic Fluids Databook, British Cryoengineering Society (2002)

Special Case # 1: Hydrogen

- Exists in two molecular states:
  - orthohydrogen – nuclear spins parallel
  - parahydrogen – nuclear spins antiparallel
- At 300 K: 75% ortho and 25 % para
- At cryogenic temperatures: parahydrogen is the lowest energy state
  - Conversion from ortho to para is slow and exothermic
- H_2 liquefiers typically include a catalyst (e.g. nickel silicate) to speed up conversion
- Thermodynamic properties of ortho and para hydrogen are significantly different

Special Case #2 : Helium
Liquid Helium exhibits quantum properties

- Requires high pressure for solidification
  - Why ?
  - The zero point energy associated with the Heisenberg Uncertainty Principal ($\Delta P \; \Delta X \sim h$) for helium at room pressures is greater than the energy required to melt helium. Thus, it won't solidify.
  - Roughly 20 Atm of pressure are required.
  - The fact that Helium remains a liquid all the way down to 0 K has significant technological advantages
- Helium has a second liquid phase (He II)
  - This come about as a result of some of the atoms condensing into the lowest ground state (very similar to Bose-Einstein Condensation)
  - Is a second order phase transition: thus no latent heat is required
  - He II (aka superfluid helium) has many unique & useful properties
  - More information in a later lecture

P-T Diagram for Helium