Lecture 2
Properties Of Cryogenic Fluids

J. G. Weisend II
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 \((h \text{ (J/kg))})\): \(h = u + Pv\)
- Entropy \((s \text{ (J/Kg K)})\): 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

- **Isentropic Expansion**: changing from high to low pressure along a line of constant entropy
- **1st Order Phase Transition**: A change in phase in which there is a discontinuity in the specific heat and which requires latent heat
- **2nd Order Phase Transition**: No discontinuity in specific heat and no latent heat is required
# Some Key Parameters of Cryogenic Fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Normal Boiling Point (K)</th>
<th>Triple Point (K)</th>
<th>Critical Temperature (K)</th>
<th>Critical Pressure (kPa)</th>
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</thead>
<tbody>
<tr>
<td>Krypton</td>
<td>119.8</td>
<td>115.8</td>
<td>209.4</td>
<td>5496</td>
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<tr>
<td>Methane</td>
<td>111.6</td>
<td>90.7</td>
<td>190.6</td>
<td>4599</td>
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<tr>
<td>Oxygen</td>
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<td>54.4</td>
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<td>Argon</td>
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<td>83.8</td>
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<td>Nitrogen</td>
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<td>126.3</td>
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<tr>
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<td>Hydrogen</td>
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<td>13.8</td>
<td>32.9</td>
<td>1283.8</td>
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<tr>
<td>Helium</td>
<td>4.2</td>
<td>N/A</td>
<td>5.2</td>
<td>227.46</td>
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</table>
Generic T-S diagram Showing Isenthalps, Isobars and 2 Phase Region
T-S Diagram for Nitrogen

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T S Diagram illustrating a Refrigeration Cycle
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
• 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
  – GASPAK & HEPAK from CryoData
    [http://www.htess.com/software.htm](http://www.htess.com/software.htm)
  – An interactive website also from NIST should suffice for this class
Additional Sources for Cryogenic Fluids Data

  - This is a detailed bibliography for cryogenics material properties and includes fluids
- **Thermodynamic Properties of Cryogenic Fluids**, R. Jacobson et al.,
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
- H₂ 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 comes 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