1.3 Properties of Cryogenic Fluids

What are the properties for cryogenic fluids that are important to system engineering?

- State Properties
 - Phase Diagrams
 - Equations of State (imperfect gases)
 - Condensed phase properties (ρ , β , κ , C_p , h_{fg} , and σ)
 - Optical, electric and magnetic properties
- Transport properties
 - Thermal conductivity & viscosity (k, μ)
 - Prandtl number (Pr = $\mu C_p/k$)

These properties depend on the molecular configuration and inter-molecule interactions

See Chapter 2: Barron, <u>Cryogenic Systems</u>

Phase diagram of common fluid system

- Phase diagram is a 3D map of the Equation of State for an element or compound.
- Regions and points of interest in Cryogenics.
 - Critical point (T_c, p_c, v_c)
 - Phase co-existence
 - Normal boiling point (NBP)
 - Triple point (TP)
 - Subcooled liquid
 - Supercritical gas
 - Solid state



Common Cryogenic Fluids



Properties of Cryogenic Liquids

	Liquid	Liquid	Liquid	Liquid nitrogen ^a	Liquid air	Liquid fluorine	Liquid argon	Liquid oxygen ^b	Liquid methane
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Normal boiling point (K)	4.224	20.268	27.09	77.347	78.9	85.24	87.28	90.18	111.7
Density (kg/m ³)	124.96	70.78	1204	808.9	874	1506.8	1403	1141	425.0
Heat of vaporization									
(kJ/kg)	20.73	445.6	86.6	198.3	205.1	166.3	161.6	212.9	511.5
Specific heat (kJ/kg K)	4.56	9.78	1.84	2.04	1.97	1.536	1.14	1.70	3.45
Viscosity (kg/m \cdot s \times 10 ⁶)	3.57	13.06	124.0	157.9	168	244.7	252.1	188.0	118.6
Thermal conductivity									
$(mW/m \cdot K)$	27.2	118.5	113	139.6	141	148.0	123.2	151.4	193.1
Dielectric constant	1.0492	1.226	1.188	1.434	1.445	1.43	1.52	1.4837	1.6758
Critical temperature (K)	5.201	32.976	44.4	126.20	133.3	144.0	150.7	154.576	190.7
Critical pressure (MPa)	0.227	1.293	2.71	3.399	3.90	5,57	4.87	5.04	4.63
Temperature at triple									
point (K)		13.803	24.56	63.148		53.5	83.8	54.35	88.7
Pressure at triple			10.0	10.52		0.22	60.6	0.151	10.1
point (MPa × 10 ³)		7.042	43.0	12.53	_	0.22	08.0	0.151	10.1

Table 2.1. Selected Properties of Cryogenic Liquids at Normal Boiling Point

" Reference 3.

^h Reference 1.

From Timmerhaus and Flynn, Cryogenic Process Engineering USPAS Cryogenics Short Course Boston, MA 6/14/10 to 6/18/10

Equation of State for gaseous systems

- Equation of state is a functional relationship between state properties (p, P, T)
- For gases, there exist fairly simple relationships
 - ideal gas : pv = RT
 - "real gases" e.g. Van der Waal gas
 - a intermolecular attraction
 - b hard core repulsion
 - Virial Expansion
 - Models that include quantum effects
 - Quantum virial expansion (helium)
 - H₂ gas
 - Compressibility factor (Z = pv/RT) is a measure of the deviation from ideal gas behavior (Z = 1 for ideal gas)
 - Detailed numerical codes for properties of cryogenic fluids (e.g. REFPROP) use fits based on equations of state compared to experimental data

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$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$$
$$pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + \dots\right)$$

Law of Corresponding States

Assumes that the equation of state is universal about the reduced critical point:

$$\frac{p}{p_c} = \Phi\left(\frac{T}{T_c}, \frac{v}{v_c}\right)$$

 Φ is a universal function

- Assumptions
 - No quantum effects (poor assumption for He, H₂ and Ne)
 - Spherical molecule, neglects polarity effects (H₂O, CO₂, etc.)
- The Law is based on assumption: Isobar has an inflection point at T_c

Mathematically, an inflection point has the property:

$$\frac{\partial p}{\partial v}\Big|_{T_c} = \frac{\partial^2 p}{\partial v^2}\Big|_{T_c} = 0$$



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Van der Waal's Equation of State

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$$

- This is a simple "real gas model" that can account for some phenomena such as liquefaction and the Joule Thomson effect
- From the law of corresponding states, the VdW equation of state predicts that $b = 1/3v_c$ and $a = 9/8RT_cv_c$

Fluid	T _c (K)	p _c (MPa)	a(m ⁶ kPa/kmol ²)	b(m³/kmol)	T _{Bo} (K)
Helium	5.2	0.227	3.46	0.0237	17.6
Hydrogen	33.2	1.315	24.4	0.0262	112
Neon	44.5	2.678	21.5	0.0173	149
Nitrogen	126.2	3.396	137	0.0386	427
Oxygen	154.6	5.043	138	0.0318	522

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Virial Expansion Equation of State

- The Virial expansion is useful for detailed analysis.
- General form $pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + ...\right)$
 - B is the second virial coefficient and represents corrections due to 2-body interactions
 - C is the third virial coefficient for 3-body interactions
- Virial coefficients can be calculated using knowledge of the interparticle interactions
 - Second classical virial coefficient:

• Interparticle interactions are given by approximate potentials, $\phi(r)$, which describe the attractive or repulsive force between two molecules (more later on this)

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Compressibility Factor for Real Gases



- Z = 1 for ideal gas but can be > or < 1 for real gases.
 - Z > 1, p > p(ideal gas) as result of finite particle size
 - Z < 1, p < p(ideal gas) meaning that the particle attraction reduces the pressure
- Boyle Temperature:
 - T_{bo}= pv/R
 - where Z = 1



Thermodynamic Properties

- Tds = dE + pdv (Differential form of 1st and 2nd Law)
- The heat capacity is defined as the change in the heat content with temperature.

$$C_{v} = T \frac{ds}{dT}\Big|_{v} = \frac{\partial E}{\partial T}\Big|_{v} \qquad \qquad C_{p} = T \frac{\partial s}{\partial T}\Big|_{p}$$

 These two forms of the heat capacity are related through the following thermodynamic relationship

$$C_p - C_v = -T \frac{\partial v}{\partial T} \Big|_p^2 \frac{\partial p}{\partial v} \Big|_T = \frac{T v \beta^2}{\kappa}$$
 for gases where $C_p - C_v \sim R$

 Enthalpy, h, is a useful thermodynamic property for quantifying heat content of a fluid.

h = E + pv and in differential form, dh = Tds + vdpso the specific heat is also given as $C_p = \frac{\partial h}{\partial T}\Big|_p$ USPAS Cryogenics Short Course Boston, MA 6/14/10 to 6/18/10

State Properties Summary (T-S Diagram)



Lines of constant h are called "isenthalps" Lines of constant p are "isobars"

Transport properties

- Transport properties (viscosity & thermal conductivity) are fundamental to cryogenic process engineering
 - Viscosity (μ or ν): involved in mass transport behavior
 - Thermal conductivity (k): heat transport property
- Most transport properties of fluids are empirically determined:

Laminar flow:



Fourier's law:
$$Q = -kA \frac{dT}{dx} \approx kA \frac{\Delta T}{t}$$



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Examples of transport properties (REFPROP)



- Viscosity
 - Gas region μ ~ Tⁿ, n ~ 0.5
- Thermal conductivity
 - Gas region k ~ Tⁿ, n ~ 0.5
- Prandtl number

• Gas:
$$\gamma = C_p/C_v = 7/5$$
 (diatomic)

$$\Pr = \frac{\mu C_p}{k} = \frac{4\gamma}{9\gamma - 5} = 0.74$$

Liquids Liquid $T(\mathbf{K})$ Pr 2.20 77 N_2 90 2.21 O_2 H_2 20.4 1.17 H_2O 311 4.52 0.004 Hg 750 1.15 He 4.2 4/10 to 6/18/10 13

Hydrogen

- Diatomic Molecule (H₂)
- Isotopes:
 - Ordinary hydrogen has only one proton in nucleus
 - Deuterium has one p and one n in nucleus and is 1 part in 1600 of all natural occurring H
 - Tritium has one p and two n in nucleus and is radioactive with a half life of 12.26 years
- Natural forms (H_2, HD, D_2) ; HD much more abundant than D_2 . Why?
- Applications for cryogenic hydrogen
 - Rocket fuel ($LH_2 + LO_2$)
 - Transportation (vehicle fuel systems + gO₂)
 - Detectors in high energy physics experiments
 - Semiconductor processing (high purity H₂ gas)
 - Nuclear fusion reaction processes (D_2 and T_2)
 - ITER Project

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Molecular states of hydrogen

 Molecular hydrogen can exist is two different states depending on <u>nuclear spin</u>



Ortho-hydrogen

Para-hydrogen

- Normal hydrogen is in equilibrium at ambient temperature with 75% ortho and 25% para (called nH_2). All states equally populated
- At 20.4 K = NBP, equilibrium concentration is 99.8% para and 0.2% ortho.
- Equilibrium concentration is a function of temperature.
- Conversion is exothermic and must be catalyzed to accelerate conversion
- Deuterium also has O-P conversion, but $n\text{-}D_2$ is 2/3 ortho and 1/3 para- D_2

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Ortho-Para Conversion of H₂

- Ortho-para conversion is an exothermic process
 - ∆E_{op}(20K) ~ 700 kJ/kg
 - Compared to heat of vaporization, h_{fg} ~ 445 kJ/kg
- Equilibrium concentration is a function of temperature
 - 25% Para @ 300 K
 - ~ 50% Para @ 80 K
 - 99+% @ 20 K
- Conversion is slow as it depends on 3-body interactions
- For long term storage of LH₂, need to complete O-P conversion

Equilibrium concentration is a function of temperature



Temperature (K)

Ordinary O-P conversion

- If the reaction that convert Ortho hydrogen to Para hydrogen is not catalyzed, then it occurs rather slowly
- Reaction rate,

$$\frac{dx_o}{dt} = -C_2 x_o^2$$

Where x_o is the ortho fraction and C_2 = 0.0114 hr⁻¹ is the rate constant

- Since the rate is proportional to x_o^2 , the reaction will slow as the conversion proceeds
- The heat deposited as a result of the conversion is proportional to this rate

$$Q_{op} = h_{op} \frac{dx_o}{dt}$$

Where does the Q_{op} go?



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Storage losses of unconverted H₂







At t = 0, 100% liquid H_2 with the designated fraction of para- H_2 .

The fraction lost is due to conversion from ortho to para heating and vaporizing the liquid.

Catalysis of O-P Conversion



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Catalyzed O-P conversion

- If the reaction that convert Ortho hydrogen to Para hydrogen is catalyzed, then it occurs much more rapidly
- Reaction rate,

$$\frac{dx_o}{dt} = -C_1 x_o$$

Where x_o is the ortho fraction and C_1 is the rate constant that depends on the type of catalyst used

 As before, the heat deposited as a result of the conversion is proportional to this rate

$$Q_{op} = h_{op} \frac{dx_o}{dt}$$

Where does the Q_{op} go?



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Ortho/Para Conversion of H₂

How to know if the o-p conversion is complete?



- Uses hydrous ferric oxide (Fe(OH)₃) catalyst
- Ortho/para ratio determined based on ~3% difference in vapor pressures of $p-H_2$ and $n-H_2$ (75% ortho + 25% para)

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T-S Diagram for Para H₂



Entropy (kJ/kmol-K)

Heat Capacity of Gaseous H₂

- At high temperature C_v/R ~ 5/2 (diatomic molecule)
 - 3 translational degrees of freedom
 - 2 rotation
- At low temperature, rotation is suppressed, C_v/R ~ 3/2



From Barron, Cryogenic Systems

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Transport properties of H₂ (Refprop)



 Transport properties similar to other diatomic molecular liquids

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Liquid Hydrogen

- e-H₂ properties:
 - T_{nbp} = 20.3 K
 - Density = 70.8 kg/m³
 - h_{fq} = 446 kJ/kg
 - $T_c = 33 \text{ K}$
 - P_c = 1.3 MPa
 - T(Triple pt) = 13.8 K
 - P(Triple pt) = 7 kPa
- Vapor pressure depends on fraction ortho-para (about 5% effect)
- Other phases (HD & D₂)



Molecular volumes of solid and liquid hydrogen, deuterium, and hydrogen deuteride under saturation conditions [31].

Specific heat of liquid hydrogen



Isotopes (H_2, HD, D_2) have different transition temperatures. Example, freezing point of H_2 , D_2 and HD



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Hydrogen Summary

- Liquid hydrogen is the lowest density liquid (SG = 0.07)
- Ortho-para conversion process is unique in fluids
- Three isotopes of interest (H, D, T)
- Easily oxidized to produce significant energy

 $H_2 + O_2 \implies H_2O + energy$

Safety issues (to be discussed later)



Helium

- Inert, spherical molecule is the closest approximation to an ideal gas
- Helium is about 0.1 ppm in the atmosphere
- Obtained in separation process in natural gas (~ 0.2% concentration)
- Two stable isotopes (He⁴ and He³, which is 0.1 ppm of natural helium)
- Quantum effects are important at low temperatures (T < 20 K)
 - He⁴ obeys Bose-Einstein statistics (nuclear spin = 0)
 - He³ obeys Fermi-Dirac statistics (nuclear spin = $\frac{1}{2}$)
- Approximate forms of the equation of state
 - Van der Waal's gas model not suitable at low temperature due to quantum effects
 - Virial expansion including quantum phenomena
- Tabulated properties for He⁴ (Refprop[®] or HEPAK[®])
- History of helium discovery (R. Longsworth)

Compressibility Factor for Helium



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Equations of State

- Helium is the closest approximation to an ideal gas (pv =RT)
- Helium is not well described by the "Law of Corresponding States" because at low temperature it is not a classical fluid
- Virial expansion is a popular approximate equation of state

$$pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + ..\right)$$

B is the 2nd virial coefficient resulting from two body interactions C is the 3rd virial coefficient resulting from three body interactions

Classical 2nd Virial coefficient:
$$B_{CL} = -\frac{N}{2}\int_{0}^{\infty} \left[e^{-\phi(r)/k_{B}T} - 1\right] 4\pi r^{2} dr$$

where $\phi(r)$ is the effective particle interaction

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Molecular Potentials





- Oscillating dipole moment due to electron distribution in molecule
- Momentary weak attraction
- Hard core repulsion
- For helium:
 - ε₀/k_b = 10.22 K
 - $r_0 = 0.255 \text{ nm}$
 - r_m = 0.287 nm

Lennard Jones potential

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Quantum Gas Models

- Quantum fluids (like He, H₂) have behavior that deviates from classical making ordinary equations of state unusable
- Quantum Virial expansion requires solution to wave equations and scattering theory
 - Difficult calculation
 - Beyond scope of course
- Example: Second virial coefficient for helium
- Empirical fit to data

$$B_{qu}(T) = a - \frac{b}{T}$$

 $a = 23.05 \text{ cm}^3/\text{mole}$ $b = 421.77 \text{ cm}^3\text{K}/\text{mole}$



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Example: Pressure of He gas

Consider a container with a known mass of helium gas.
Calculate the pressure.



Given:

- m = mass of helium gas
- T = absolute pressure (K)
- V = volume of container (m³)
- Solution using suitable equation of state



T-S Diagram for Helium



Entropy (kJ/kmol-K)

Liquid Helium

Phase diagram



Two Liquid phases

- He I Neutonian fluid
 - T_λ < T < T_c = 5.2 K, P_c = 0.226 MPa
- He II quantum fluid
 - T < T_λ = 2.176 K @ SVP
 - T_{λ} (solid line, 3 MPa) = 1.76 K
- Solid phase only under external pressure P > 2.5 MPa
- Important point: no triple point

Density of Liquid Helium



Density (ρ)

- ρ_{critical} = 70 kg/m³
- ρ_{NBP, 4.2 K} = 125 kg/m³
- $\rho_{max, 2.2K} = 146 \text{ kg/m}^3$
- ρ ~ constant (T < 2.2 K)
- Co-existing vapor density
 - The density of helium vapor is high compared to co-existing vapor for other fluids. Why?

• ρ_{vapor} (4.2 K) ~ 15 kg/m³

Thermal Properties



- Heat Capacity
- Entropy
- Heat of Vaporization (h_{fq})





Transport properties of normal helium



- Viscosity, (μ)
- Thermal conductivity (k)
- Prandtl number, $Pr = \mu C_p/k$



Transport properties much different in He II regime

Unique properties of superfluid helium (He II)

- State properties (C, s, h_{fg})
- Unique behavior in the transport peoperties
 - Viscosity
 - Heat conductivity
 - Sound propagation
 - Film flow
 - Fountain effect

Viscosity of He II

- Viscosity depends on method of measurement
 - As measured by a rotating disk, μ is finite
 - As measured by flow through a capillary, $\mu \sim 0$
- Physical explanation
 - Viscosity of the normal fluid component drags with disk
 - Superfluid is invisid, so it can flow through the capillary
- The explanation of this behavior is integral to the "Two Fluid" model for He II



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Heat Conductivity of He II

- Anomalous heat transport
 - Effective heat conductivity comparable to that of high purity metals
 - Low flux regime dT/dx ~ q
 - High flux regime dT/dx ~ q³
 - Transition between two regimes depends on diameter of channel
- Heat transport in He II can be understood in terms of the motion of two interpenetrating fluids. This "Two Fluid" model effectively describes the transport properties



Sound Propagation in He II



He II Film Flow

Rollin film (1937):

- Saturated film exists on all surfaces above the liquid
- Unique aspect of He II is that the film is mobile (flows)
- Siphon driven by hydrostatic head difference
- Two containers with different levels will tend to equalize

<u>Film thickness</u>

$$d \sim \frac{K}{y^n}$$

 $n \sim 0.4$ $K \sim 3 \ge 10^{-6} \text{ cm}^{0.6}$





Fountain Effect

- Due to the invisid nature of the superfluid, it can flow through microscopic channels without friction
- Ideal "superflow" conserves chemical potential, $\Delta p = \rho s \Delta T$
- Components to Fountain pump:
 - Heater provides chemical potential difference
 - Porous plug allows only invisid superfluid component to flow
 - With the heater on, the superfluid flows into the bulb through the porous plug
 - Normal fluid can not flow out through plug since it is viscous
 - Normal fluid builds pressure and leaves the top





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Summary: Cryogenic Fluid Properties

- Cryogenic fluid properties are mostly known and available
 - Refprop (NIST database)
 - HEPAK (commercial data base for helium)
- Properties of cryogenic fluid mixtures are not as well known, but are of technical interest (cryocoolers)
- Superfluid helium (He II) properties are unique
 - Inviscid flow
 - Very high heat conductivity