CRYOGENIC ENGINEERING

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Lecture No - 3

Overview of Earlier Lecture

- What is Cryogenics and its applications
- Temperature Scales
- Cryogens, Properties, T – s Diagram
  - Argon
  - Air
  - Nitrogen
  - Neon

Outline of the Lecture

- Hydrogen
- Ortho and Para forms of Hydrogen
- Helium
- Phase diagram of Helium

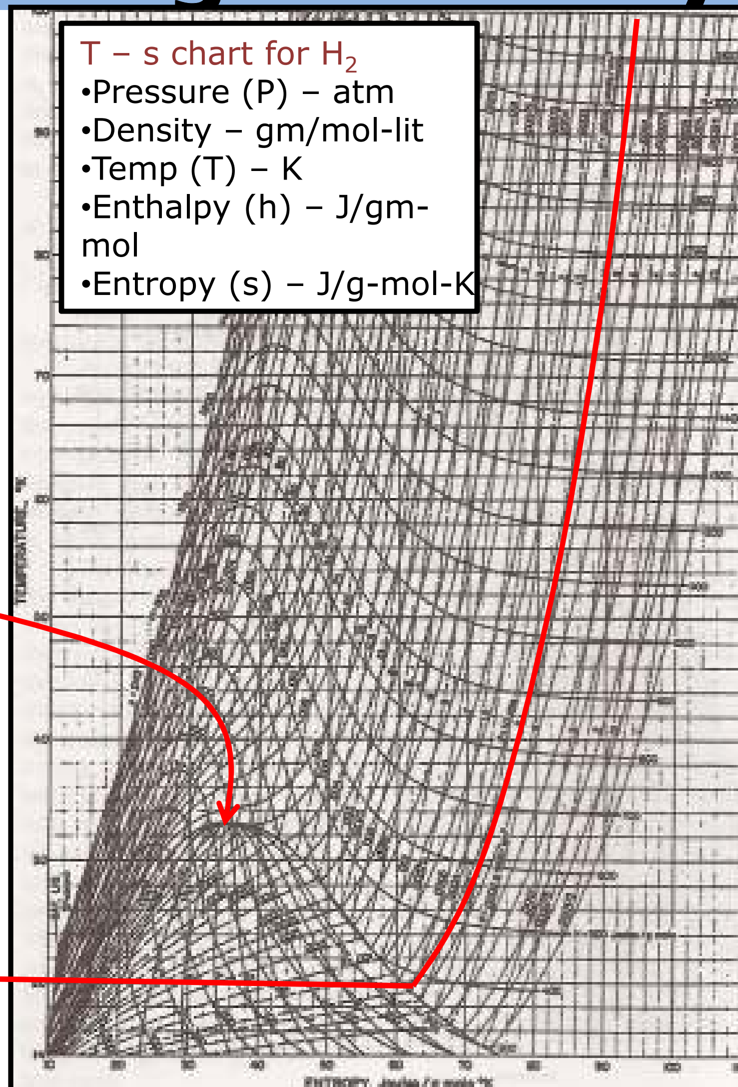
Hydrogen

Hydrogen

- Hydrogen exists in diatomic form as H_2.

Normal Boiling Point	K	20.27
Normal Freezing Point	K	13.95
Critical Pressure	MPa	1.315
Critical Temperature	K	33.19
Liquid Hydrogen Density	kg/m^3	70.79
Latent Heat	kJ/kg	443

T – s diagram of Hydrogen



Critical Point
13.15 atm,
33.19 K

1 atm,
20.27 K

At 1 atm

ρ_{vap} = 1.33 kg/m^3

ρ_{liq} = 70.79 kg/m^3

Hydrogen

Hydrogen

- It has three isotopes viz, hydrogen, deuterium and tritium.

Isotope	Relative %	Atomic Mass (1p+n)
Hydrogen	6400	1+0
Deuterium	1	1+1
Tritium	Very rare	1+2

- Tritium is radioactive and is unstable with a T_{half} as 12.5 years.

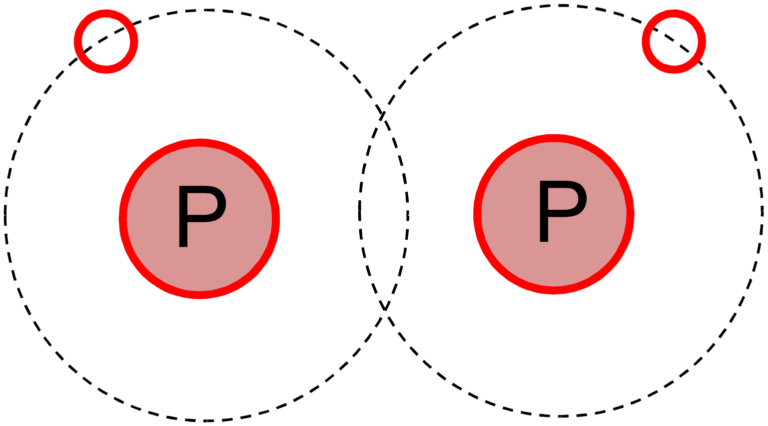
Hydrogen

Hydrogen

- The relative ratio of existence of hydrogen as diatomic molecule (H_2) and as Hydrogen Deuteride (HD) is 3200:1.

- Hydrogen exists in two molecular forms - Ortho and Para.

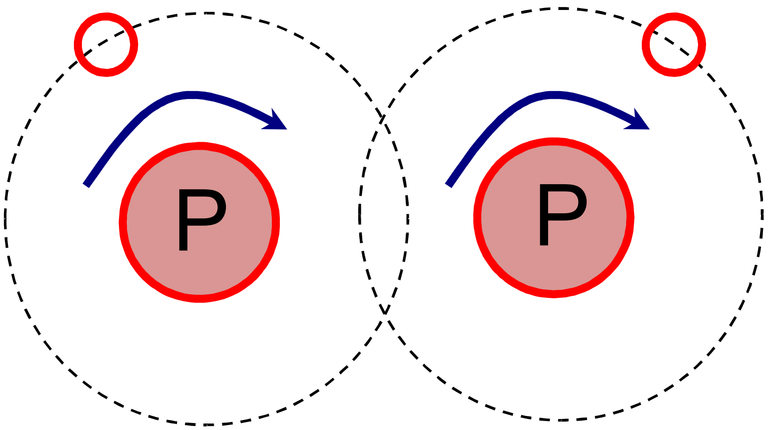
Ortho & Para Hydrogen



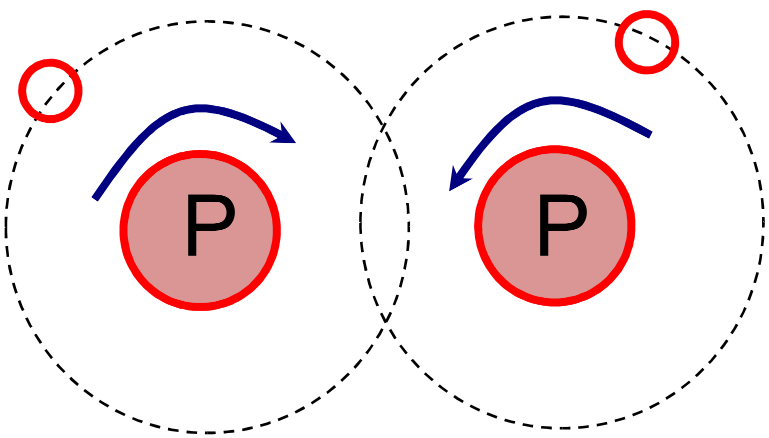
- Spin is defined as a rotation of a body about its own axis.
- A H_2 molecule has 2 protons and 2 electrons.
- The distinction between the two forms of hydrogen is the direction of the spin of protons.

Ortho & Para Hydrogen

Ortho - Hydrogen



Para - Hydrogen



- The two protons possess a spin which gives the angular momentum.
- If the nuclear spins are in same direction for both the protons, it is Ortho Hydrogen.
- If the nuclear spins are in opposite direction for both the protons, it is Para Hydrogen.

Hydrogen

Hydrogen

- With the decrease in the temperature, the Ortho hydrogen is converted to the Para hydrogen.

At 300 K	
Form	Relative %
Ortho	75
Para	25

At 20 K	
Form	Relative %
Ortho	0.179
Para	99.821

Hydrogen

- Para form is a low energy form and therefore heat is liberated during conversion.
- Conversion of ortho to para form of hydrogen is an exothermic reaction.
- This conversion is a very slow process.
- In order to make this conversion faster, catalysts are added.

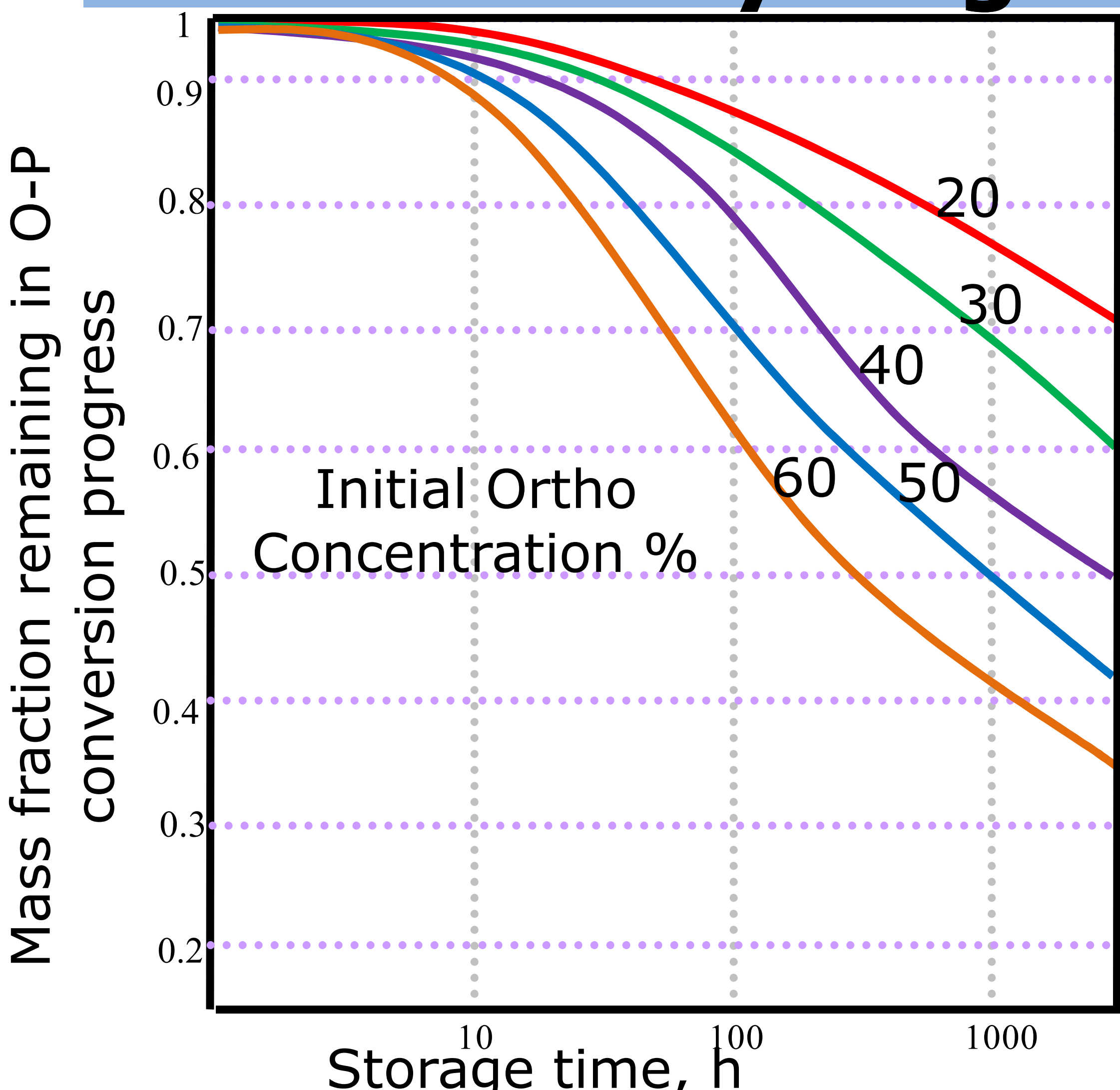
Hydrogen

Liquefaction

- During liquefaction, the heat of conversion causes evaporation of 70% of hydrogen originally liquefied.

- This is an important constraint in liquefaction and storage of H_2.

Hydrogen



- Figure showing the fraction of liquid H_2 evaporated due to Ortho to Para conversion with storage time.
- Hence, liquefaction of hydrogen should ensure complete conversion.

Deuterium

- Deuterium atom has one proton and one neutron. Two Deuterium atoms make up one D_2 which is called as Heavy Hydrogen.
- Similar to hydrogen, it also has different spatial orientations - Ortho and Para forms.
- The relative concentration of these two forms is a function of temperature.
- Normal deuterium exists in ratio of 2/3 Ortho and 1/3 Para.

Deuterium

- As temperature decreases, Para D_2 gets converted to Ortho D_2. (In case of hydrogen, Ortho H_2 gets converted to Para H_2).

At 300 K	
Form	Relative %
Ortho	66.67
Para	33.33

At 20 K	
Form	Relative %
Ortho	98.002
Para	1.998

- Most of the physical properties of Hydrogen and Deuterium mildly depend on Ortho - Para Composition.

Hydrogen

Uses

- Cryogenic engines are powered by propellants like liquid hydrogen.
- It is being considered as fuel for automobiles.
- Cryocoolers working on a closed cycle use hydrogen as working fluid.
- Hydrogen codes and standards should be followed to ensure safety while handling liquid hydrogen.

Helium

Helium

- Evidence of Helium was first noted by Janssen during solar eclipse of 1868. It was discovered as a new line in the solar spectrum.

- In the year 1895, Ramsay discovered Helium in Uranium mineral called as Clevite.

- In the year 1908, K. Onnes at Leiden liquefied Helium using Helium gas obtained by heating Monazite sand procured from India.

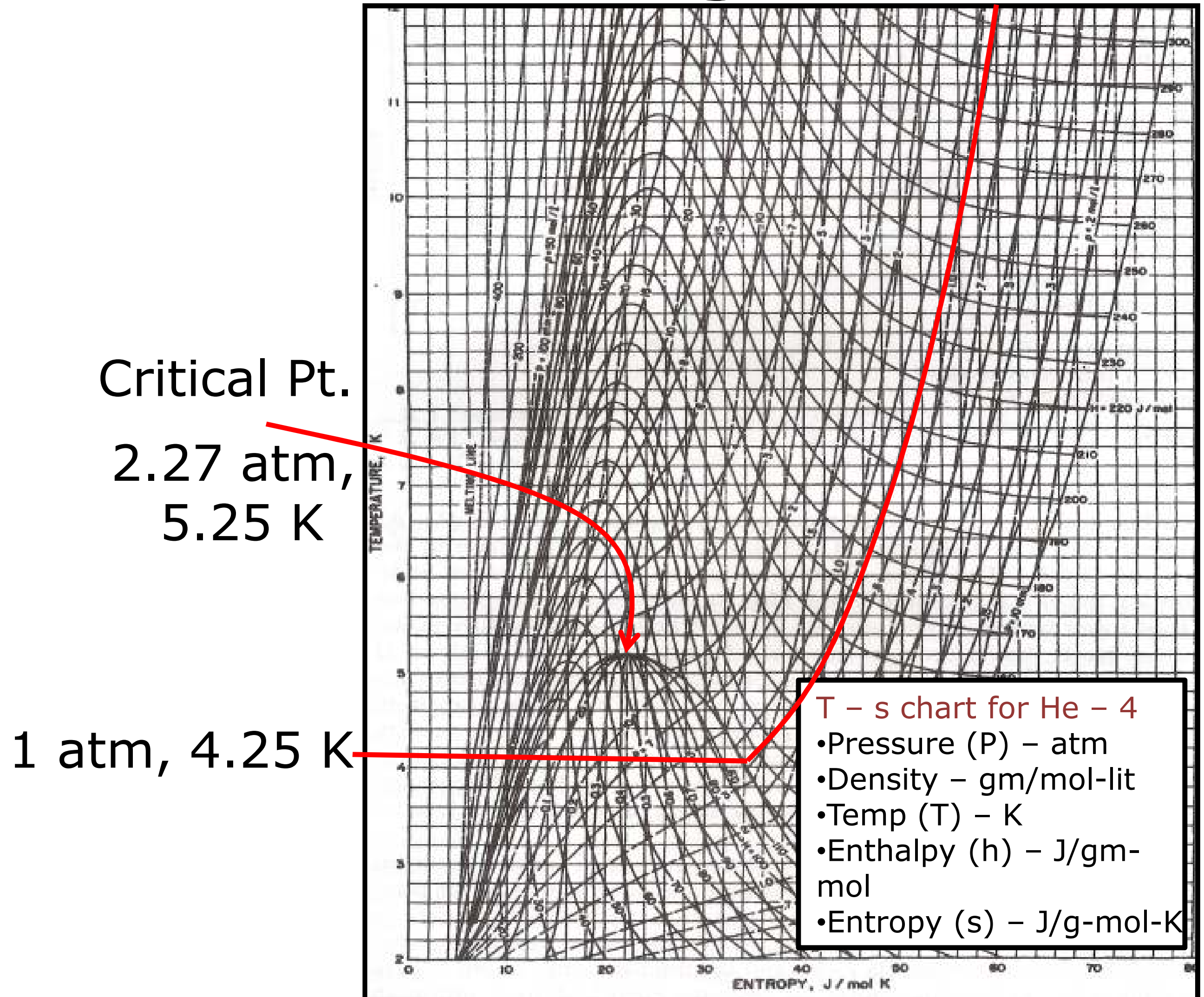
Helium

Helium

- Helium is an inert gas and exists in monatomic state.

Normal Boiling Point	K	4.25
Normal Freezing Point	K	NA
Critical Pressure	Mpa	0.227
Critical Temperature	K	5.25
Liquid Helium Density	kg/m^3	124.8
Latent Heat	kJ/kg	20.28

T – s diagram of Helium



At 1 atm

ρ_{vap} = 16.87 kg/m^3

ρ_{liq} = 124.8 kg/m^3

Helium

Helium

- In 1920, Aston discovered another isotope of Helium - He^3 in addition to He^4.
- Helium exists in two isotopes.
  1. He^4 = 2 electrons, 2 protons + 2 neutrons.
  2. He^3 = 2 electrons, 2 protons + 1 neutrons.

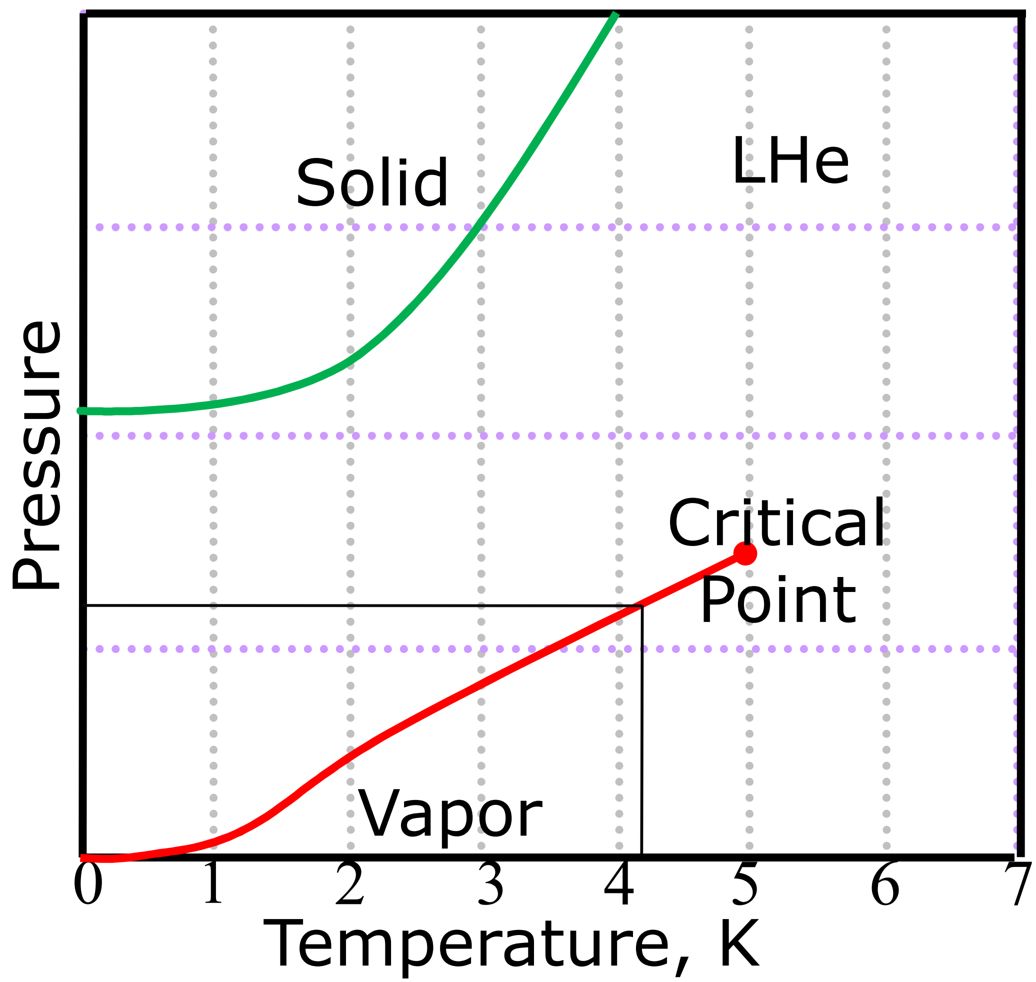
Helium

Helium

- The percentage of He^3 is 1.3 x 10^{-4} %. So mostly it is He^4.

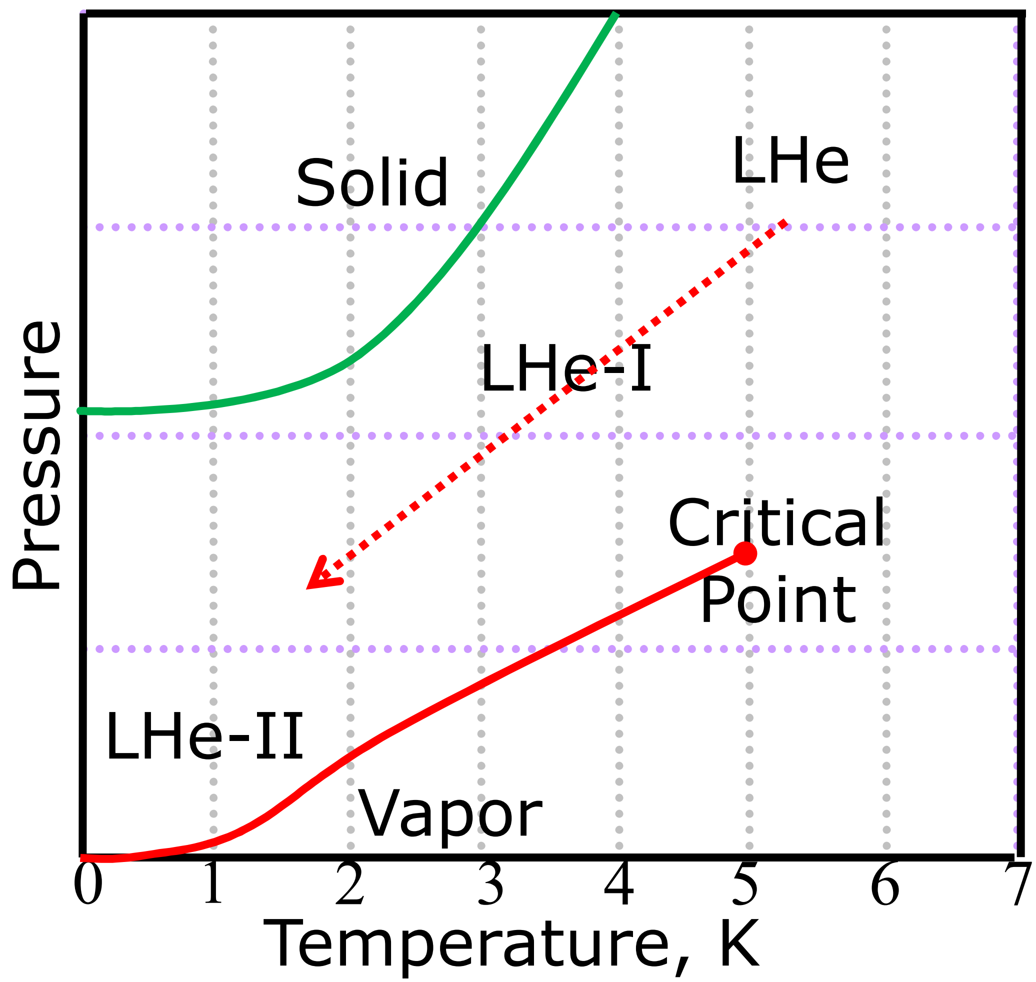
Isotope	Relative %
He – 4	~100
He – 3	1.3 x 10^{-4}

Helium Phase Diagram



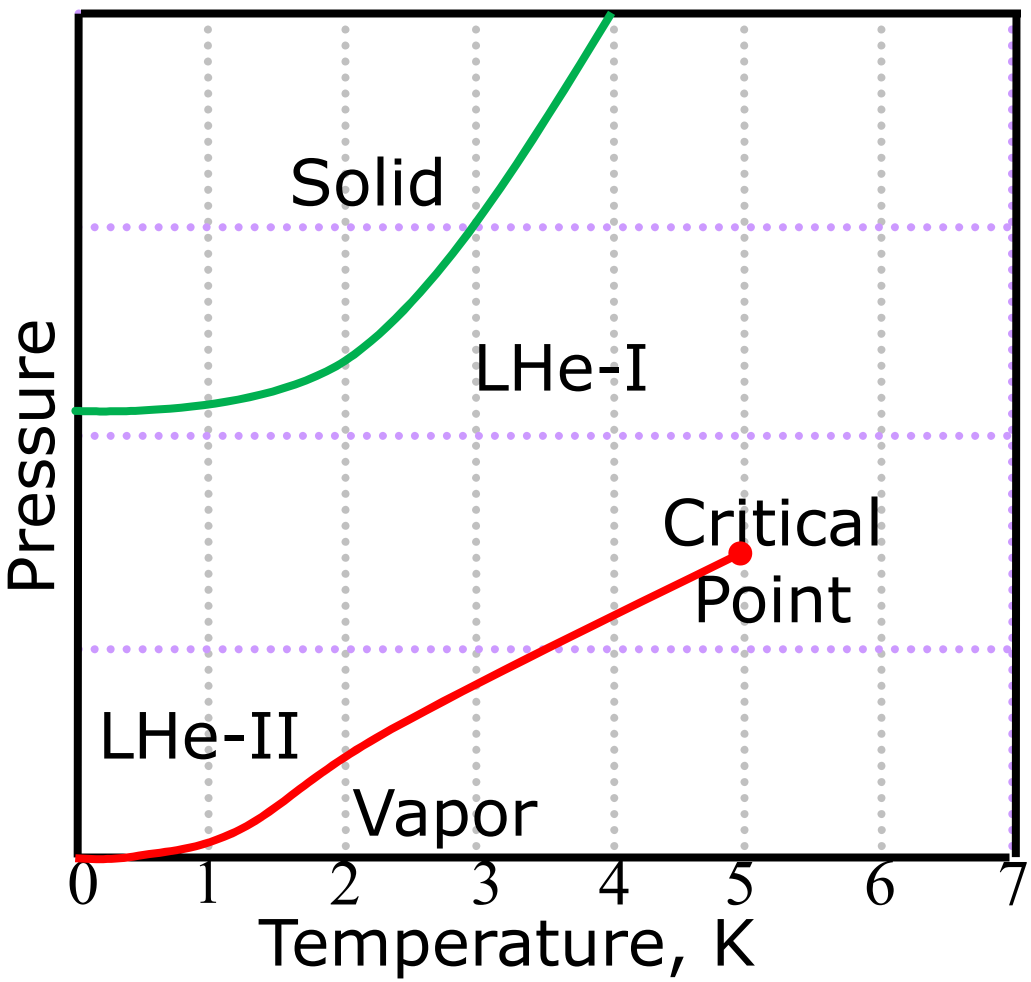
- From the adjacent figure, Helium has no temperature and pressure at which solid - liquid – vapor can co-exist. It means that it has no triple point.
- Saturated liquid Helium must be compressed to 25.3 bar to solidify.

Helium Phase Diagram



- As Liquid Helium is further cooled below a particular temperature (2.17 K)
- A new liquid phase, LHe–II, emerges out.
- The two different liquids are called as LHe – I and LHe – II.

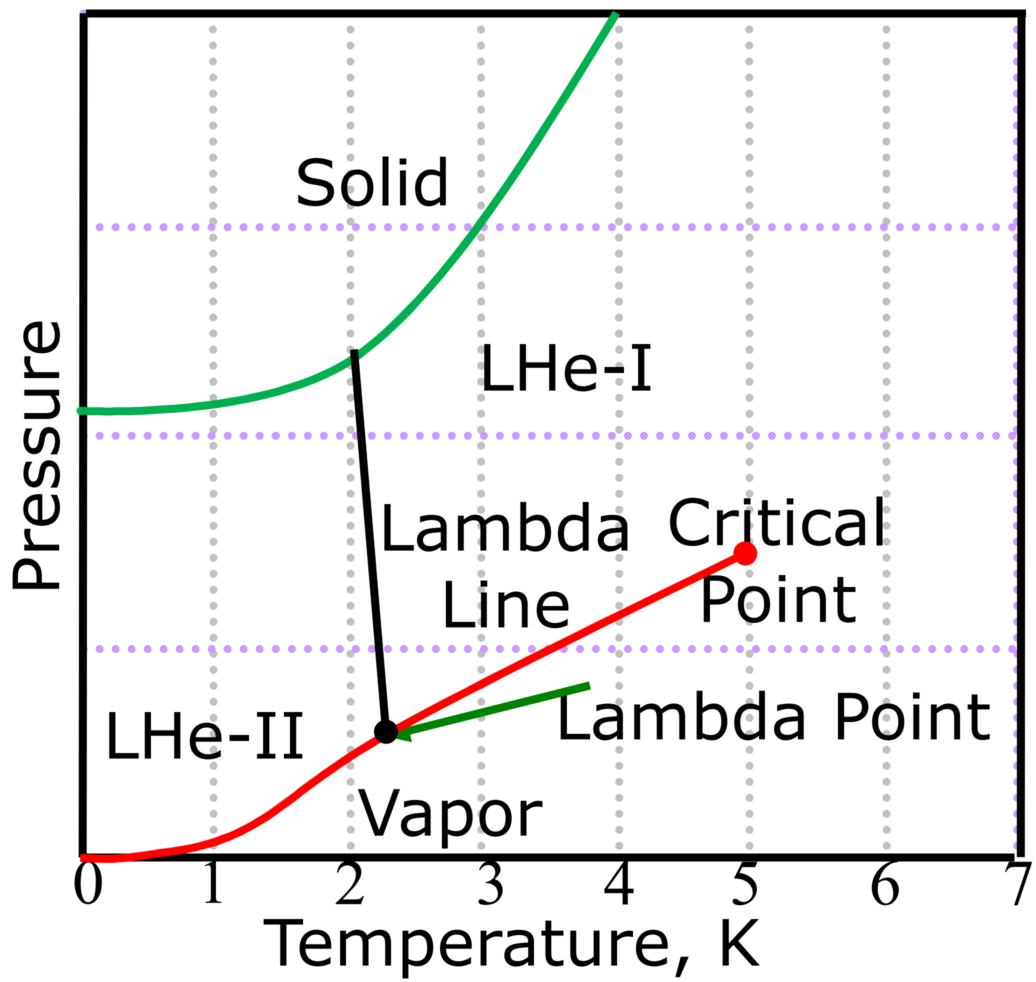
Helium Phase Diagram



- These liquid phases are distinguished on the basis of viscosity as follows.

- LHe–I : Normal fluid
- LHe–II : Super fluid

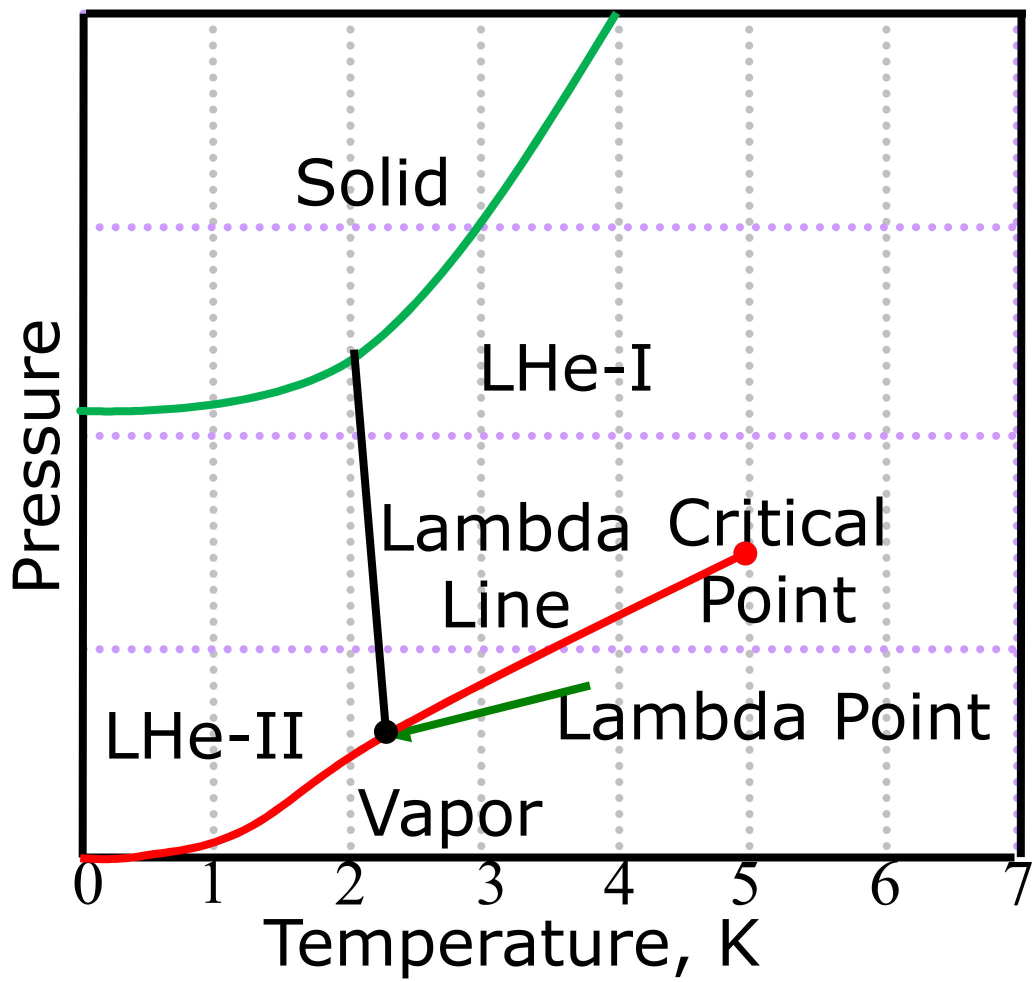
Helium Phase Diagram



- This phase separation line is called as Lambda Line.

- The point of intersection of phase separation line with saturated liquid line is called as Lambda Point.

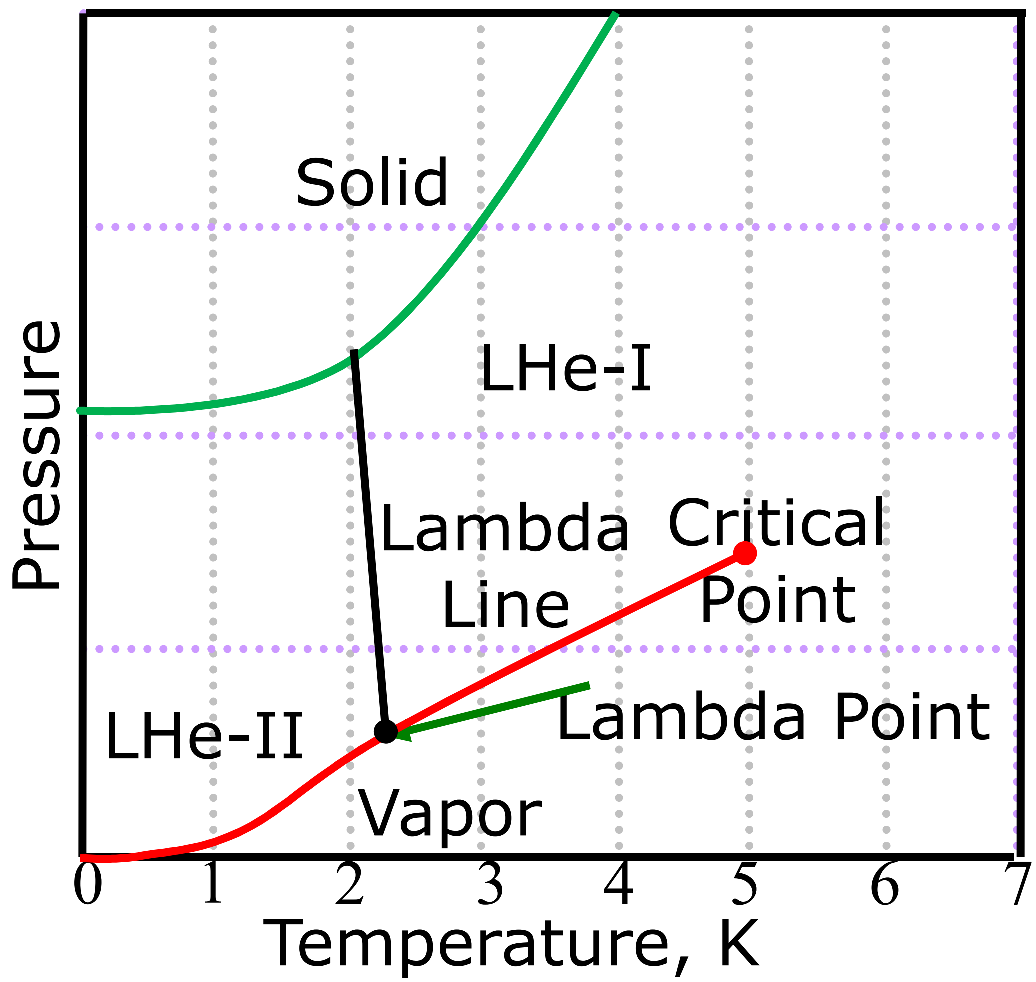
Helium Phase Diagram



- LHe – II is called as super fluid because it exhibits properties like zero viscosity and large thermal conductivity.

- This fluid expands on cooling.

Helium Phase Diagram



- Owing to its low viscosity, the fluid below the lambda point, LHe – II, flows through narrow slits and channels very rapidly.

Phase Transition

First Order

$$G = E + PV - TS$$

- The first order derivative of Gibbs Free Energy w.r.t. pressure at constant temperature gives density.

- The density undergoes an abrupt change leading to a discontinuity called as Gibbs First Order discontinuity or 1st Order Transition.

Phase Transition

First Order

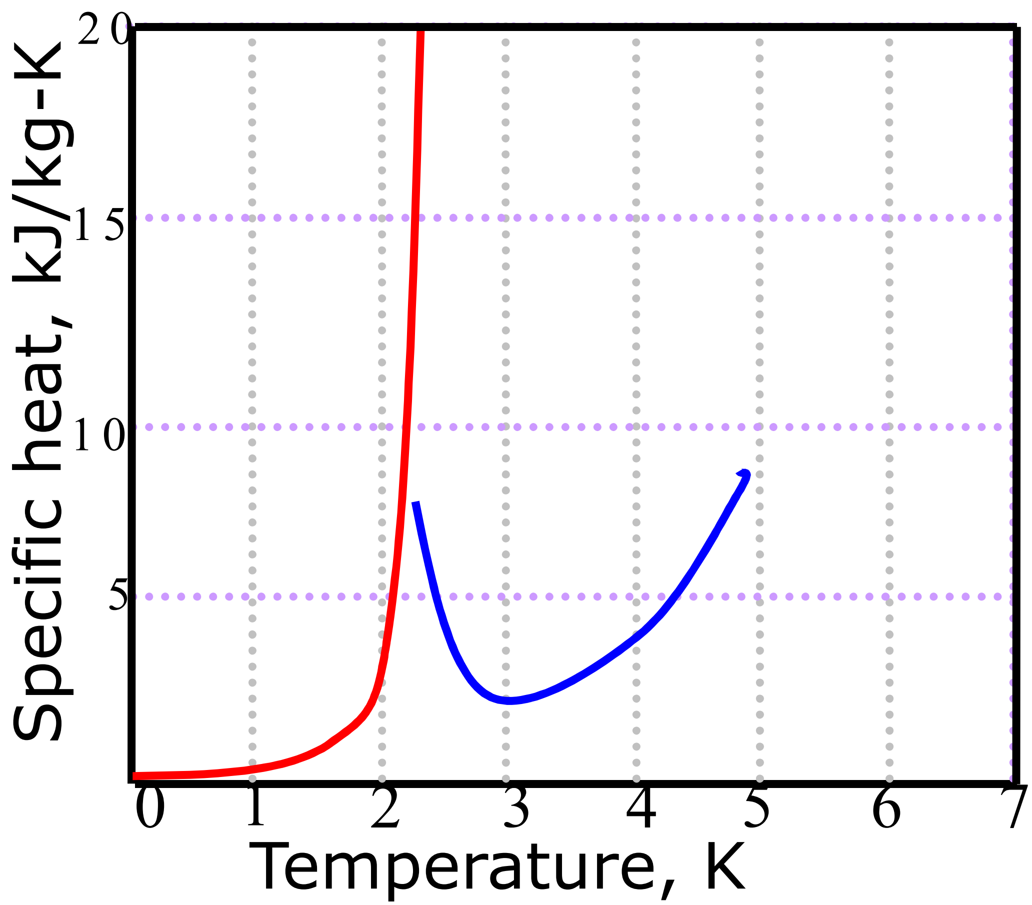
- These transitions involve latent heat.
- The temperature of the system remains constant.
- For example, the solid to liquid or liquid to gaseous transition, the latent heat is absorbed at constant temperature.

Phase Transition

Second Order

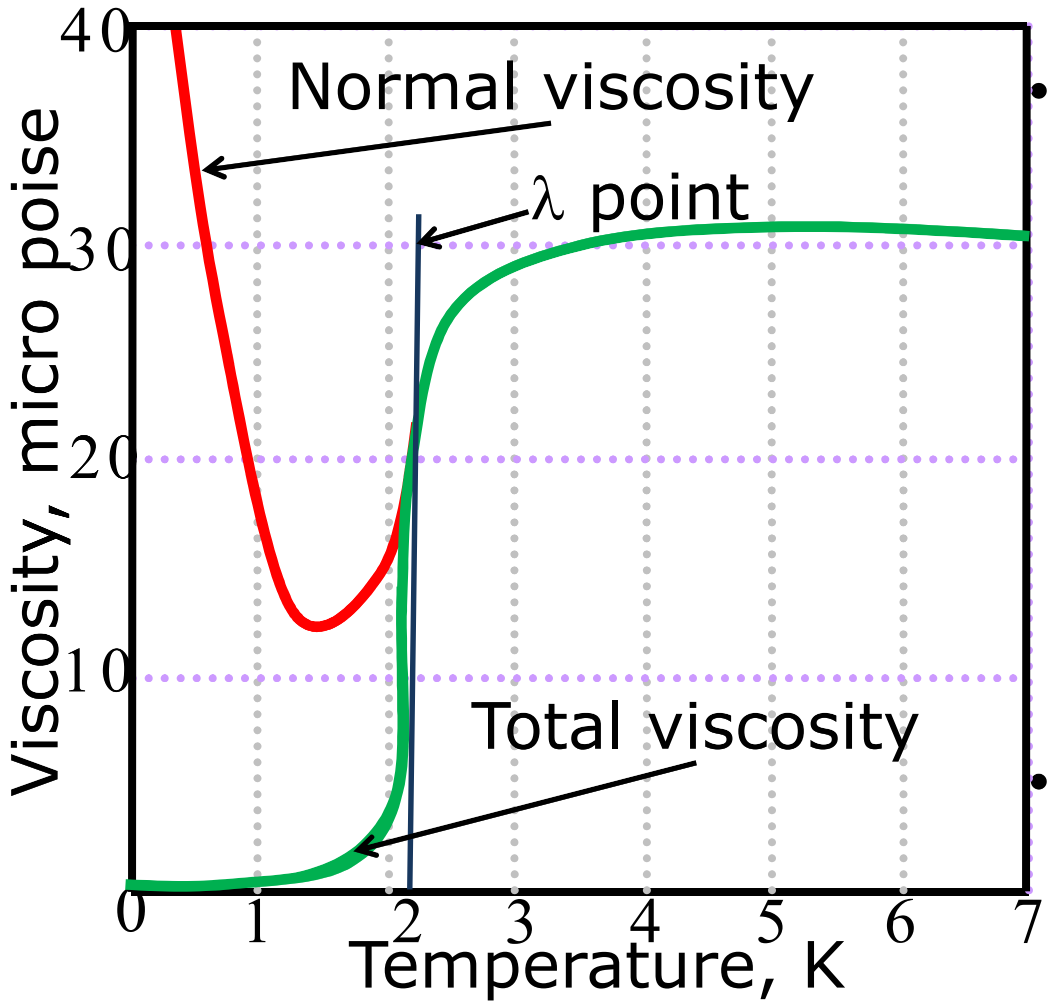
- These transitions are continuous in first order but exhibit discontinuity in second order.
- The second derivative of Gibbs free energy w.r.t. chemical potential gives the specific heat.
- The variation of specific heat in Liquid Helium is abrupt and posses a discontinuity at the lambda point.

Phase Transition



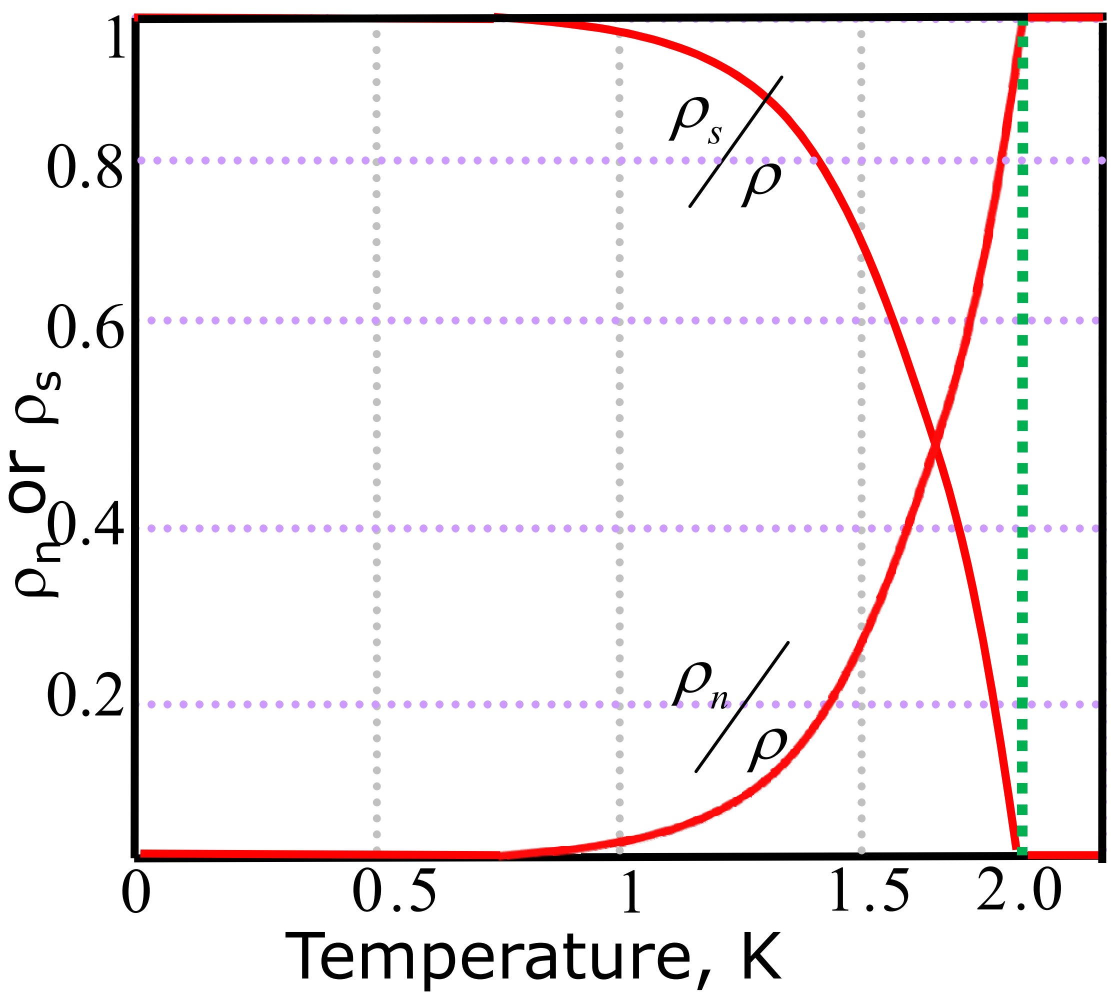
- The point is called as lambda point because shape of the curve resembles the Greek letter λ .
- There is no energy involved in lambda transition.
- Specific heat is infinite at λ point and it is called as 2nd Order Transition.

Super fluid Helium



- Kapitza et al. stated that viscosity for flow through thin channels is independent of pressure drop and is only a function of temperature.
- To explain this anomaly, a two fluid model is used.

Super fluid Helium

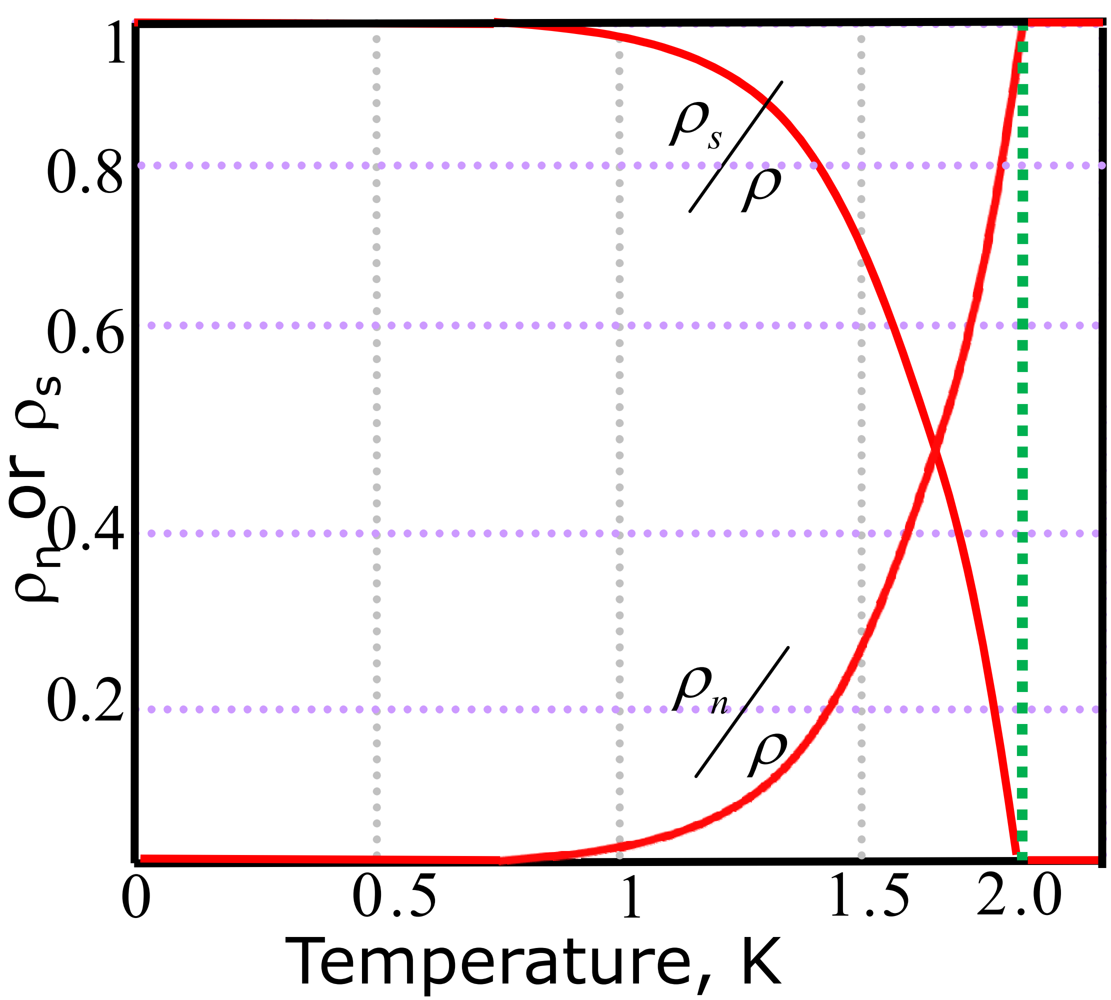


- In the two fluid model, the liquid is assumed to be composed of two fluids, normal and super fluid.

- Mathematically,
  $\rho = \rho_n + \rho_s$

  ρ - total density
  ρ_n - normal density
  ρ_s – super fluid density.

Super fluid Helium



- The figure shows the temperature dependence of density below lambda point.

T	ρ
=0	$= \rho_s$
$\geq$ 2.17	$= \rho_n$
0 to 2.17	$= \rho_n + \rho_s$

Super fluid Helium

- Also, heat transfer in super fluid helium (LHe – II) is very special. When the pressure above LHe - I is reduced by pumping, the fluid boils vigorously.
- During pumping, the temperature of liquid decreases and a part of the liquid is boiled away.
- When T < λ point temperature, the apparent boiling of the fluid stops.

Super fluid Helium

- Liquid becomes very clear and quiet, even though it is vaporizing rapidly.
- Thermal Conductivity of He – II is so large, that the vapor bubbles do not have time to form within the body of the fluid before the heat is quickly conducted to the surface.

Fluid	Thermal Cond. (W/m-K)	Viscosity (Pa s)
He – I	0.024	3×10^{-6}
He – II	86500	10^{-7} to 10^{-12}

Information

Kaptiza was awarded Nobel Prize in Physics in the year 1978 for his basic inventions and discoveries in the area of low – temperature physics.

- A self assessment exercise is given after this slide.
- Kindly asses yourself for this lecture.

Self Assessment

1. Boiling point of Hydrogen is ____________
2. Isotopes of hydrogen are _______, ________ & __________
3. H_2 with same proton spin is characterized as ________ hydrogen
4. As temperature decreases, Deuterium converts from _____ to ______
5. A new phase of LHe begins at _________

Self Assessment

6. Viscosity is zero at __________
7. Boiling point of Helium is __________
8. The thermal conductivity of He – I and He – II are ________ and ___________ respectively.

Answers

1. 20.3 K
2. Hydrogen, Deuterium and Tritium.
3. Ortho Hydrogen
4. Para, Ortho
5. 2.17 K
6. Lambda point
7. 4.2 K
8. 0.024, 86500

Thank You!