

Cryogenic Engineering
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Module No. # 01
Lecture No. # 03
Properties of Cryogenic Fluids

Welcome to the third lecture on cryogenic engineering. I will just briefly take an overview of what my earlier lectures were.

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

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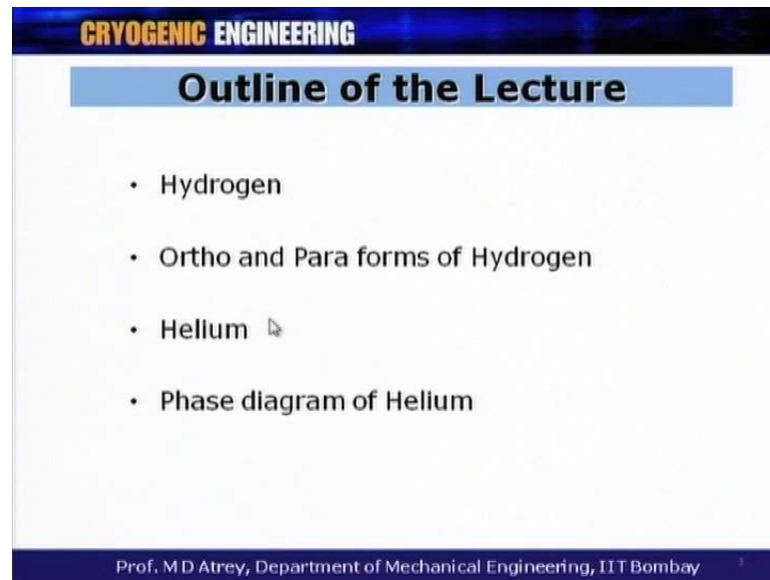
In the first lecture we talked about what cryogenics was, and we discussed various applications of cryogenics in space, in superconducting, in mechanical engineering, and in medicine, and things like that.

In the last lecture, which was the second lecture, we talked about different temperature scales, and we also concluded from that, one can positively use Kelvin scale, it is for our benefit, so that we do not have to say every time minus 100 and 96 degree centigrade, and we can always say - 77 Kelvin, using this temperature scale.

We also talked about various cryogenics; we talked about their properties, and we talked about the importance of T - s diagram that is temperature entropy diagram. We found that from the temperature entropy diagram lots of things can be understood. We can

understand what the boiling point is, what the critical point is, how the enthalpies vary with temperature, how the entropy varies, and how different pressures and temperatures vary. We discussed different cryogenics and their properties in brief, of argon, air, nitrogen, and neon.

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The slide features a dark blue header with the text "CRYOGENIC ENGINEERING" in white and yellow. Below the header is a light blue bar with the title "Outline of the Lecture" in bold black text. The main content area is white and contains a bulleted list of four items: "Hydrogen", "Ortho and Para forms of Hydrogen", "Helium", and "Phase diagram of Helium". At the bottom of the slide is a dark blue footer with the text "Prof. MD Atrey, Department of Mechanical Engineering, IIT Bombay" in white.

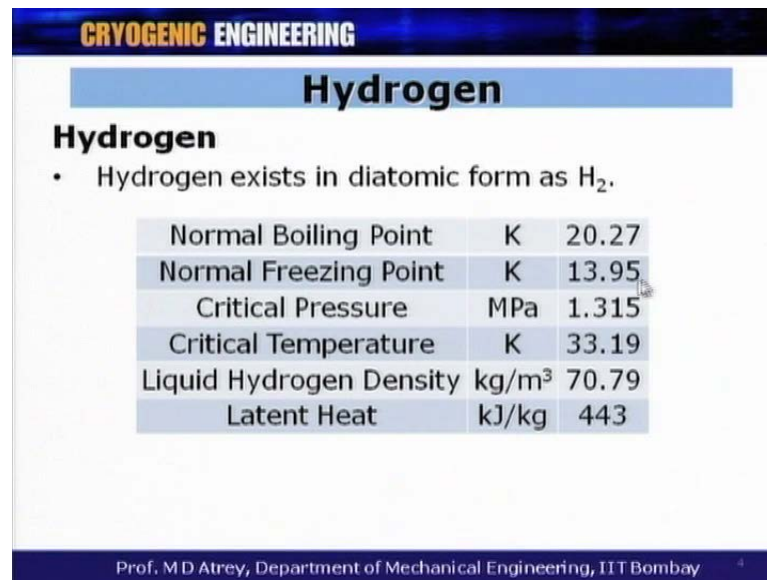
- Hydrogen
- Ortho and Para forms of Hydrogen
- Helium
- Phase diagram of Helium

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Here we got a feel of various cryogenics, and what I am going to talk about today is cryogenic hydrogen. We talked about the specialty of hydrogen; that is, Ortho and Para forms of hydrogen. What are these different forms? What is it all about? We will see in this lecture. Helium is a very special gas, it is a very useful gas in cryogenic engineering, and we will discuss the Phase diagram of Helium. What are the different phases in helium? How do they co-exist, and things like that?

In my last lecture where I talked about cryogenics, we had written one statement over there that - hydrogen and helium are special cryogenics, and therefore, they will be dealt specially in a special lecture. This is the special lecture, in which we want to talk about hydrogen and helium. In fact, we will continue talking about helium in the next lecture also.

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CRYOGENIC ENGINEERING

Hydrogen

Hydrogen

- Hydrogen exists in diatomic form as H₂.

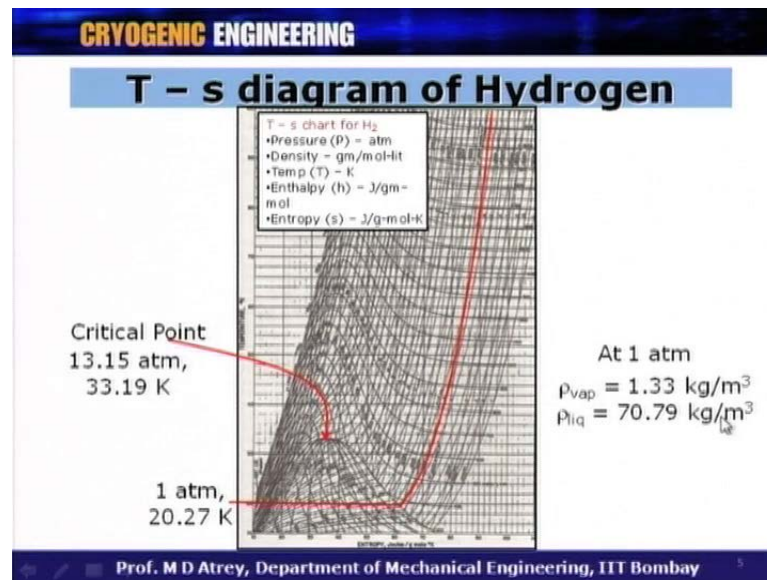
| | | |
|-------------------------|-------------------|-------|
| Normal Boiling Point | K | 20.27 |
| Normal Freezing Point | K | 13.95 |
| Critical Pressure | MPa | 1.315 |
| Critical Temperature | K | 33.19 |
| Liquid Hydrogen Density | kg/m ³ | 70.79 |
| Latent Heat | kJ/kg | 443 |

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Let us go up to hydrogen, which has got its boiling point at 20 Kelvin. Hydrogen exists in diatomic form as hydrogen, everybody knows about this; and these are the normal properties of hydrogen gas. What are its properties? It has got a normal boiling point of 20.27 Kelvin at one bar, one atmosphere. It has a normal freezing point of 13.95 Kelvin. It has a critical pressure of 1.315 MPa, or around 13 bar pressure. It has a critical pressure of 33 Kelvin, that is, 33.19 Kelvin to be exact.

Now, it has got a density of 70.79 kg per meter cube, and the latent heat is 443 Kilo Joule per kg, when it gets converted from gas to liquid or, from liquid to gas. These are very important properties; and this means that I can use liquid hydrogen to give me a cooling effect at around 20 Kelvin approximately, or above. I cannot come below 20 Kelvin. If I have to come, and use hydrogen at temperature lower than 20 Kelvin, then I have to remove the pressure over it; that means, I have to go into vacuum to touch down lower and lower temperature, and at 13.95 Kelvin, liquid hydrogen will get converted into solid hydrogen.

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This is the temperature entropy diagram of hydrogen. I always told you that, all the mechanical engineers or all the cryogenic engineers first should refer to T - s diagram to understand different property variations with temperature. So, on the y axis what we have is the temperature, and what x axis what you have got is an entropy. You may not be able to see properly, it is possible; but, just have a look at different lines on this diagram. For example, you can see the dome over here; it means that, inside this dome what you have is a 2 phase mixture, that is, liquid plus vapor. You can see all these lines which are coming from the top to the bottom; it means, they are all isobaric lines, that is, the pressure remaining constant. You can see all these curved lines; they are all isenthalpic line, or the enthalpy remaining constant.

Why I am stretching this point is, when you go in the next lectures, when you go for liquefier and refrigeration, we will deal with these diagrams in every problem. We have to understand the property variation, enthalpy variation, and entropy variation at every point, and for that, we will always have to refer to the T - s diagram of different gases, or different cryogenes.

So here, you can see a line which is at one bar, and this is the temperature corresponding to the change of phase from gas to liquid, or nothing but the boiling point of hydrogen, which is one atmosphere pressure and 20.27 Kelvin as the temperature. Now this is the

critical point, and the properties of critical point are – 13.15 atmospheres and 33.19 Kelvin temperature. So, this is the critical temperature, and this is the critical pressure.

In addition to that, I have just given data to understand the density of vapor at one atmosphere in the saturated condition, which is 1.33 kg per meter cube, and that of liquid is 70.79 kg per meter cube hydrogen.

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CRYOGENIC ENGINEERING

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.

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Now, some general information about hydrogen - it has 3 isotopes hydrogen, deuterium, and tritium. The relative percentage of existence of these 3 isotopes is 6,400 and 1 for hydrogen and deuterium respectively. The atomic mass in this case is, all these things have got 1 proton in the nucleus, and the number of neutrons will vary depending upon what isotope we are talking about, for example, for hydrogen we have got 0 neutron, for deuterium we have got 1 neutron, and for tritium what we have is 2 neutrons. Now, this tritium is a very rare substance, a very rare gas in comparison to what you see for hydrogen and deuterium.

In addition to that, the tritium gas is a radioactive gas, and is unstable with a half life of 12.5 years. So, whenever we have to deal with tritium, one has to be very, very careful. One has to worry about all its radioactivity and all the measures have to be taken, to deal with this tritium. In fact, this is not normally used in commercial operations. What normally we will use is - hydrogen of course, and sometimes we can have deuterium as heavy water, etcetera. We will come to that later.

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CRYOGENIC ENGINEERING

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.

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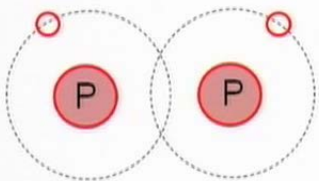
The relative ratio of existence of hydrogen as diatomic molecule, that is, hydrogen H_2 , and as Hydrogen Deuteride, sometimes hydrogen is like H_2 or HD, as deuterium item gets combined to form hydrogen deuteride – HD, and the relative ratio is 3,200:1.

Now, the important fact about hydrogen is that, it exists in 2 molecular forms, that is, Ortho and Para. So, we have got an Ortho form, and we have got a Para form. This is very important; and we will talk about this Ortho and Para forms of hydrogen with a little bit detail in the coming slides.

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CRYOGENIC ENGINEERING

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.

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So, what is this Ortho and Para hydrogen? Well before I really go into Ortho, and Para, etcetera. I will talk about some third parameter called 'spin'; because, from this definition of spin, we understand what Ortho hydrogen is, and what Para hydrogen is. So, what is the spin? The spin is defined as the rotation of a body about its own axis. We know the earth spins, we know it (()) while on the earth. When it rotates, it spins about its own axis.

So, this is what I am talking about hydrogen molecule, and you have got 2 atoms of hydrogen together, which means you have got 2 protons. So, hydrogen molecule has 2 protons and 2 electrons.

These protons will be spinning all the time. The distinction between the 2 forms of hydrogen is what we talked about as Ortho hydrogen, and Para hydrogen, is basically because of the direction of the spin of these protons. So, as I have just said these 2 protons will have some spin, and what is the direction of that spin? With it we will decide if it is a Ortho hydrogen, or if it is a Para hydrogen. As soon as we talk about Ortho and Para, lot of properties associated with the energy of hydrogen will get decided; and we will talk about that in the next slide.

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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.

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The 2 protons possess a spin, which gives the angular momentum. Possibly, I talked about DC MRI system also. You have got hydrogen molecule, and this proton immediately gets aligned to the magnetic field because of the spin.

Similarly, I am talking about the same thing here. The 2 protons possess a spin, and this gives the angular momentum, which will have a direction. So here, you can see 2 protons, and you can see 2 clockwise directions over here, which indicate the spin of these protons.

If the nuclear spins are in the same direction for both the protons, it is what we call Ortho hydrogen; that means, if both of them are in the same direction, clockwise in this case, it is nothing but Ortho hydrogen. If you see the next slide, we have got 2 protons, 2 atoms of hydrogen together. One has a spin in this direction, and one has a spin in the opposite direction. So, one is clockwise, and other one is anti-clockwise. This is what we call as Para hydrogen.

So essentially, if the nuclear spins are in the opposite direction for both the protons, it is Para hydrogen, and if both the spins are in the same direction, we call it Ortho hydrogen. So, it is just the difference of spin of the protons, which makes it Ortho or Para.

Now what happens? Why are we studying all these? As soon as you start lowering the temperature of the hydrogen gas, this Ortho will start getting converted to Para; that means, the molecules, which had the spin in the same direction, will now have the spins in the opposite direction.

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CRYOGENIC ENGINEERING

Hydrogen

Hydrogen

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

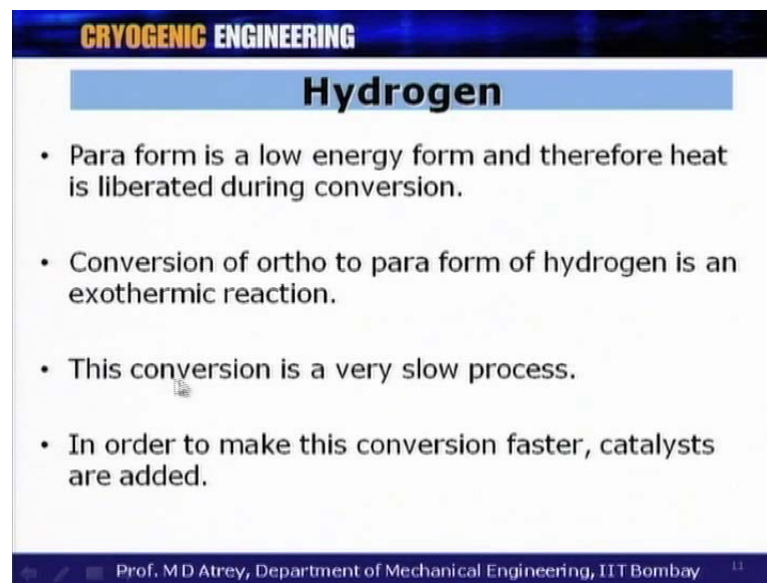
| At 300 K | | At 20 K | |
|----------|------------|---------|------------|
| Form | Relative % | Form | Relative % |
| Ortho | 75 | Ortho | 0.179 |
| Para | 25 | Para | 99.821 |

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So, with the decrease in the temperature, the Ortho hydrogen is converted to Para hydrogen. What is happening as you lower the temperature? The gas – hydrogen, is slowly starting to get converted to liquid, and here, when we start lowering the temperature, or when we start liquefying the gas, now basically if I want to reach down to 20 Kelvin from room temperature, what will happen? Ortho hydrogen will get converted to Para hydrogen. How does that happen? What are the percentages of Ortho and Para? At 300 Kelvin, I got 75% Ortho, and I got 25% Para. At 20 Kelvin, after the whole conversion had taken place, and equilibrium hydrogen has formed, what I have got is, almost all the Ortho has got converted to Para.

So, Para hydrogen at 20 Kelvin, which is nothing but the boiling point of hydrogen, the 75 to 25 ratio has got converted to almost 100%. Only 0.179% Ortho has remained there, while Para is 99.821% here. So, almost 100% Ortho has got converted to Para. Now this is the clear distinction of what exactly happens when you go on lowering the temperature of the gas, from 300 Kelvin to 20 Kelvin. Here, Ortho gets converted to Para.

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CRYOGENIC ENGINEERING

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.

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Now, this Para form is a low energy form, and therefore, heat is liberated during conversion. This is a very important thing that, Ortho has got a higher energy form, while Para is a low energy form. So during this conversion, the heat is liberated because Ortho has higher energy, while Para has lower energy. During this transformation from

Ortho to Para, lot of heat gets liberated, which means that this is basically an exothermic reaction.

So, conversion of Ortho to Para, as one goes on lowering the temperature, is basically going to result in a release of energy; and to release of energy means, increase of temperatures, or there is a lot heat energy involved over there.

So, conversion of Ortho to Para form of hydrogen is an exothermic reaction, and this conversion is a very slow process. This is the most important point again about this conversion. Just to summarize, as you go on lowering the temperature, 75:25 Ortho will get converted to Para, which is 0.179%, and 99.8% respectively. This process of Ortho to Para conversion is an exothermic reaction, and also this conversion is a very, very slow process; it does not happen fast, it happens very, very slowly. It is very important for liquefaction that this Ortho to Para conversion takes place faster; and it is also very important that this conversion is complete during liquefaction. What will happen, we will see later; but if I want to make this process of conversion very fast, then what I have to do is, I have to add a catalyst to this reaction.

So, in order to make this conversion faster, catalysts are added. There are different kinds of catalysts; there are 3 or 4 types. They have to add it in the correct quantity, in order to convert the Ortho hydrogen to Para hydrogen as fast as possible, or to make the reaction faster.

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CRYOGENIC ENGINEERING

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 H₂.

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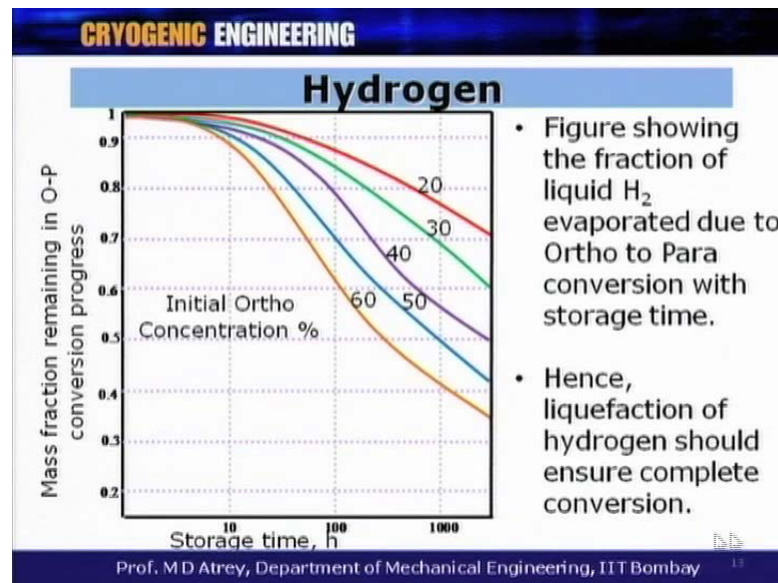
I just said, during liquefaction, the heat of conversion causes evaporation of 70% of hydrogen originally liquefied. Now this is the effect of this conversion from Ortho to Para. What is happening during liquefaction? The temperature is decreasing. What is happening because of the decrease in temperature? The heat of conversion is getting evolved, that is, it being an exothermic reaction, lot of heat is being liberated, and it evaporates; because of the effect of this heat release, whatever liquid has got formed gets evaporated immediately.

If I get the liquid, 70% of that liquid will get evaporated; because of this conversion from Ortho to Para. This is a very important constraint in liquefaction, and storage of hydrogen. So, as I said, the conversion is a very, very slow process; and if the conversion does not take place during liquefaction, I will store it in the form of liquid.

In this liquid form, this Ortho will slowly get converted to Para. During this conversion from Ortho to Para a lot of heat will get released and therefore, a lot of liquid will get evaporated. It means that, we should ensure that all the conversions happens during liquefaction only; that means, all the conversions from Ortho hydrogen, to Para hydrogen happens during liquefaction only. If that does not happen, then whatever liquid you get at the end of liquefaction, the Ortho will get converted to Para in the liquid form and therefore, it will cause the evaporation of most of the liquid that is stored. This is very, very typical of hydrogen, and this has to be taken care off.

So, what do we do? We add catalyst during liquefaction. As I just said, the catalyst makes this reaction faster, and this will ensure that the whole conversion of Ortho to Para takes place during liquefaction only, and whatever liquid has got formed will not get evaporated.

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Now, this is a graph which shows that, depending on the initial Ortho existence in the liquid, how much amount of liquid will remain at the end of so much of storage time, for example, this talks about mass fraction remaining in the Ortho to Para conversion progress, and this is the storage time on the x axis.

If I talk about this line for example, I have got liquid and this liquid has got 60% Ortho; that means, the whole conversion has not taken place during liquefaction. The liquid which I have got is stored with 60% Ortho in it. What does it mean? It means that, after so many hours, let us say, more than around 1,500 hours, what remains here is only 0.35%. Whatever original was there, only 35% of that remains. All the rest is getting evaporate; that means around 65% of the fluid has got evaporated completely.

However, if I compare this with this figure of 20, that means, my liquid hydrogen which I have got had only 20% of Ortho remaining in it; that means, 80% conversion has taken place. It has got 20% Ortho in it. At the end of around 1,500 hours, what it will have is, around 70%; that means, only 30% liquid has got evaporated during the conversion, when the initial Ortho existence was only about 20%.

Now, imagine if I had got all the conversions taken place during liquefaction; that means, my line would almost be flat line over here. If I just extrapolate this, if I say that all the conversion has taken place during liquefaction only, then over 1,500 hours this line possibly could have been at 95%, that means only 5% possibly would have got

evaporated. This shows the importance that, the liquid hydrogen I am storing should have no Ortho content, or as little Ortho content as possible. It means that, all the Ortho which was there should get converted into Para, and therefore, all the Ortho to Para exothermic reactions would take place during liquefaction only.

So, this figure shows the fraction of liquid hydrogen evaporated due to Ortho to Para conversion, with storage time. This is very important, and a big difference of hydrogen as compared all other cryogenes. Hence, we should ensure that there is complete conversion during liquefaction of hydrogen. This is what I talked about, and I am sure this is clear to you.

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CRYOGENIC ENGINEERING

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.

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The second gas or the isotope of hydrogen is deuterium. It has got 1 proton, and 1 neutron; and 2 deuterium atoms make one D_2 , which is called heavy hydrogen. So, you know D_2 is heavy water, and D_2 is what we call as the 'heavy hydrogen'.

Now similar to hydrogen, deuterium has also got Ortho and Para forms, but they are in different forms, that means, their percentages are different. The relative concentration of these 2 forms is a function of temperature. Again as it is in normal hydrogen, the normal deuterium has also got 2/3 Ortho and 1/3 Para; so, 66% is in Ortho and 33% in Para as initial case, as against 75:25 over there.

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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 | | At 20 K | |
|----------|------------|---------|------------|
| Form | Relative % | Form | Relative % |
| Ortho | 66.67 | Ortho | 98.002 |
| Para | 33.33 | Para | 1.998 |

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

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As the temperature decreases for deuterium, here, the Para D_2 gets converted to Ortho D_2 ; as against Ortho H_2 gets transmitted to Para H_2 , it is opposite that. This is just a point for comparison we are not going to talk about deuterium in detail, but I just wanted to show the comparison of deuterium behavior with that of hydrogen.

So, what happens at 300 Kelvin is, you have got 66.67% Ortho, and 33.33% of Para. At 20 Kelvin, that means, when whole thing has got converted to liquid deuterium, what you have is, almost all the Para has got converted to Ortho. So, you have got 98% Ortho, and 1.998% Para. This is the point of difference between deuterium, and hydrogen.

Most of the physical properties of hydrogen and deuterium mildly depend on Ortho and Para composition. So, whatever be the composition the physical properties do not depend so strongly on the Ortho and Para conversion.

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CRYOGENIC ENGINEERING

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.

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We have talked about the different uses of hydrogen - it is used in the cryogenic engine as a propellant, it is being considered as a fuel for automobiles. This is very important; liquid hydrogen as a fuel is very popular, and it is looked at as a future fuel by passing petrol, and diesel.

Cryocoolers working on a closed cycle, sometimes use hydrogen as a working fluid. However, one should know that hydrogen has got some safety requirements, hydrogen codes and standards should be followed to ensure safety, while handling liquid hydrogen. These are the different uses of hydrogen.

The next gas is helium. As I have explained to you about helium, this is one of the very important gases as far as cryogenic engineering is concerned. Why because, it is an inert gas, it is a non-reactive gas, and it has got a lowest possible boiling point at 4.2 Kelvin at one atmosphere; it means that, this gas will remain in a gaseous condition till 4.2 Kelvin. All other gases will get liquefied, because, their boiling points are above 4.2 Kelvin temperature, and therefore, if I want to achieve temperatures very close to 4.2 Kelvin, or below, or in the range between, let us say, 50 Kelvin to 4.2 Kelvin, I have got no other option, but the only safe, inert gas is helium. Helium has got a tremendous importance in cryogenic engineering.

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CRYOGENIC ENGINEERING

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

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The evidence of helium was first noted by Janssen, during solar eclipse in 1868. It was discovered as a new line in the solar spectrum. So, the discovery of the gas only happened around 1868.

In the year 1895, Ramsay discovered helium in a Uranium mineral called as Cleveite. So, this was the discovery on the earth for the first time, in 1895. So, you can understand that it is a gas, which is just 115 years old on the earth. In the year 1908, Kamerlingh Onnes at Leiden university liquefied helium using helium gas, which he obtained by heating Monazite sand procured from India.

So, this is the Indian connection to the first helium liquefaction that happened in 1908, by Kamerlingh Onnes at Leiden University, in Netherlands. This is a good Indian connection of which I talked about earlier, and I also told you that, the year 2008 we had the centenary year of helium liquefaction. So, all the cryogenics and physicists associated with lower temperature research, celebrated the year 2008 as the centenary year of helium liquefaction.

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CRYOGENIC ENGINEERING

Helium

Helium

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

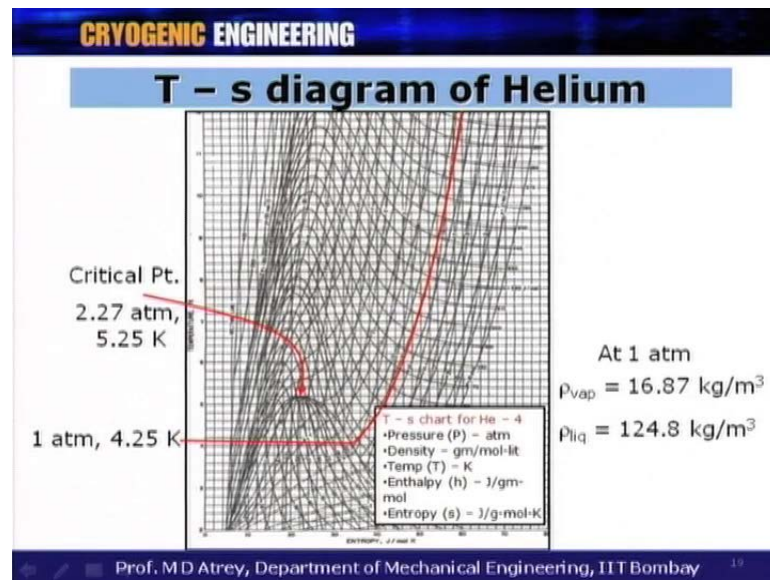
| | | |
|-----------------------|-------------------|-------|
| Normal Boiling Point | K | 4.25 |
| Normal Freezing Point | K | NA |
| Critical Pressure | Mpa | 0.227 |
| Critical Temperature | K | 5.25 |
| Liquid Helium Density | kg/m ³ | 124.8 |
| Latent Heat | kJ/kg | 20.28 |

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Helium is an inert gas, and exists in monatomic state. These are the properties of normal helium. What are they? It has got a boiling point of 4.25 Kelvin. Normal freezing point does not exist. Critical pressure it has got is 0.227 M p a, that is around 2.27 bars. Critical temperature is 5.25 Kelvin. Liquid helium density is 124.8 k g per meter cube, and the latent heat is around 20 kilo joules per k g.

20.28 kilo joule per k g is a very small latent heat; it means that, with the smallest heat coming, the liquid helium will get evaporated, and so, one has to be very careful in the usage of helium heat in ((ligs)), that happen when you use liquid helium. It is a very important parameter, because, latent heat is the one, which gives you the amount of cooling effect, or the refrigeration effect, that you want at 4.2 Kelvin.

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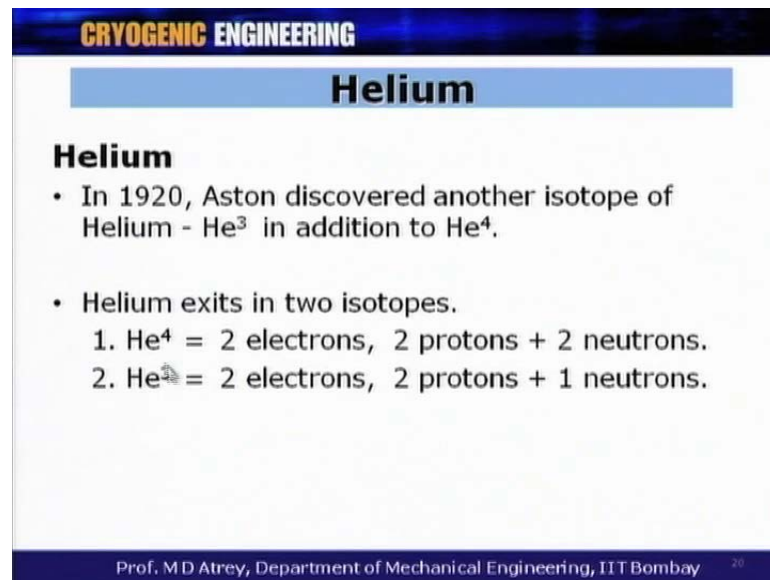


Let us see the same properties on a T - s diagram of helium. Here, you can see the dome, and this is 5 Kelvin, which means that 5.2 is a critical point over here; and what you can see again is the pressure lines - enthalpy lines, and there are also density lines. On the x axis, what you have is entropy. This is a one bar line. What you see is the boiling point of helium, which is one atmosphere and 4.2 Kelvin. This is the critical point, and the critical coordinates are 2.27 atmosphere, and 5.25 Kelvin. This information has to be known by all the cryogenic engineers.

So, whenever I say helium, or hydrogen, or nitrogen, one has to know the boiling points, and one has to know what are the critical parameters associated with those cryogenes. This is the least that is expected from a cryogenic engineer because, to know the choice of temperature, and the choice of pressure to apply, one has to have this knowledge, when we apply these cryogenes for a specific application.

Again the density for comparison sake - the density of vapor at one atmosphere in a saturated condition for helium is 16.87 k g per meter cube, and for liquid is 124.8 k g per meter cube.

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CRYOGENIC ENGINEERING

Helium

Helium

- In 1920, Aston discovered another isotope of Helium - He³ in addition to He⁴.
- Helium exists in two isotopes.
 1. He⁴ = 2 electrons, 2 protons + 2 neutrons.
 2. He³ = 2 electrons, 2 protons + 1 neutrons.

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In 1920, Aston discovered another isotope of helium, which is helium 3, in addition to helium 4. Now this isotope of helium, which is helium 3, is also very important in cryogenics; because, this is what we use in dilution refrigerator, in order to reach temperatures below 1 Kelvin. Therefore, this aspect will be covered in a next lecture. This is very important, and its discovery happened in 1920.

Helium exists in 2 isotopes. Helium 4, which has got 2 protons and 2 neutrons; and helium 3, what we just talked about, has 2 protons and 1 neutron, and that is why we call it helium 3 and helium 4, respectively.

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CRYOGENIC ENGINEERING

Helium

Helium

- The percentage of He³ is $1.3 \times 10^{-4}\%$. So mostly it is He⁴.

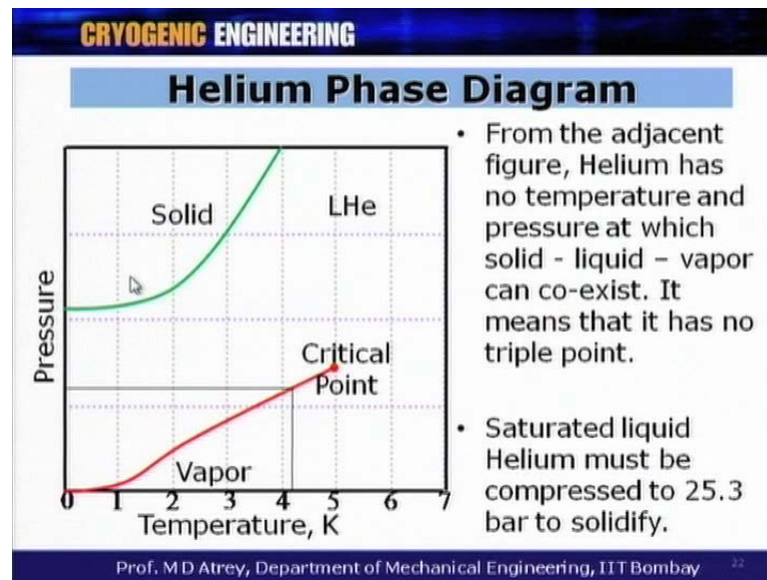
| Isotope | Relative % |
|---------|----------------------|
| He - 4 | ~100 |
| He - 3 | 1.3×10^{-4} |

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The percentage of helium 3 is very, very small - 1.3 into 10 to the power minus 4 percent. So mostly, whenever we get helium gas, it is helium 4 only. So, these terminologies are used quite frequently in helium, which is helium 4 and helium 3, and further we find in helium 1, and helium 2. These are very different ways of putting helium in very different contexts. So, one has to get used to talking about helium 4 and helium 3. When I say helium 4, it is normal helium; when I say helium 3, it is the isotope of helium 4.

So the isotope is helium 4, which as relative percentagewise is almost 100% for helium 4. Of course, there is helium 3, and its relative percentage is very small. This also means that, the cost of helium 3 is very, very high as compared to helium 4. I will not be able to tell you exact cost of helium 3, because, we could never buy that in India. However, this cost will be possibly 100 times more than that of helium 4. So, it is very costly, and therefore, its usage has to be really, properly justified.

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Now, what is important about helium is its phase diagram. This is the one of the most important aspect of helium. Try to understand this, because I am going slow, and trying to explain as much as I can on this diagram. If I want to understand about helium phase diagram, what I have is a pressure, and temperature. I am plotting the pressure and the temperature here; and what you see is a saturated vapor line - vapor pressure line, basically.

So, at 5.25 Kelvin, what you have is a critical temperature, corresponding to that, the pressure would be critical pressure. So, we have got a critical pressure, and the critical temperature. Below this what we get is a 2 phase; that is, liquid and vapor. As you know from the T - s diagram, under the critical temperature, and pressure, what you get is the liquid and vapor.

So, this is my vapor pressure line; and on this, if I give this point, it is nothing but 4.2 Kelvin and one atmosphere, which is the normal boiling temperature of helium. So, what you have here is a vapor; and what you have is the critical point, and here comes a different line which is nothing but solid hydrogen. What you have is liquid helium over here. So now, I can say that I have got 3 phases. I have got liquid helium over here, I have got vapor helium over here, and what I have here is solid helium; it means that, the liquid and vapor are coexisting together, and solid and liquid are coexisting together, but

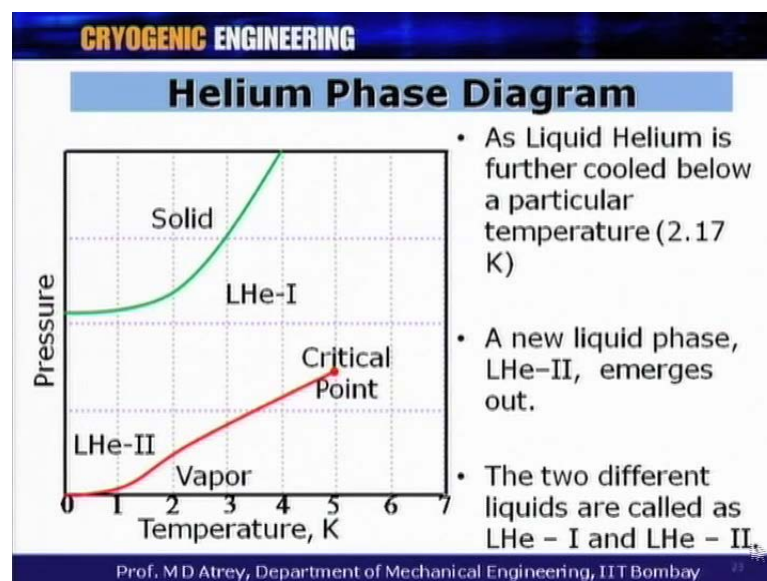
the solid, liquid and vapor are not coexisting together. This is a very important aspect of helium.

From the adjacent figure, helium has no temperature and pressure, at which solid, liquid, and vapor can coexist; it means that, it has no triple point. This is why we say that, if we go on reducing the temperature of helium it will still remain in liquid state. It will not reach the solidification point.

Now, there is a lot of physics associated with it. Helium has very high 0 point energy, something like that. It has got very involved physics, and therefore, I do not want to really go into the details of those physics aspects. For engineers, it is important understand that helium does not have a triple point, as most of other cryogenics have.

Now, what happens? Of course, solid helium does exist. So, if I want to convert something to solid helium, what will I do? I will have to pressurize this to 25.3 bar to solidify. So, saturated liquid helium must be compressed to 25.3 bar to solidify. So, this point where I can get solid, the minimum pressure is 25.3 bar. On this curve, you can see that this pressure has not been given in the scale, because this is a one bar, the pressure associated with this is around 2.5 bar, and this pressure I am talking about is now 25 bars. See, if I really want to get solid helium, I will have to compress the saturated liquid to 25.3 bar, in order to get solid helium.

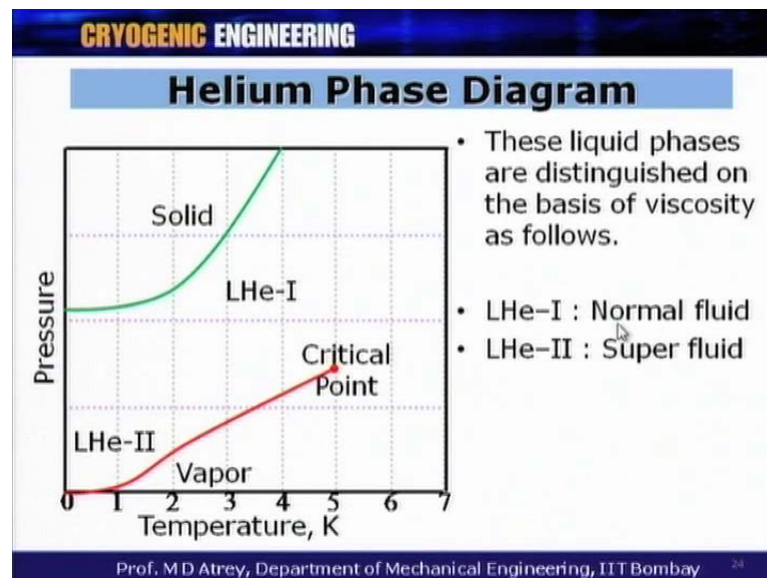
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Now, as liquid helium is further cooled, below a particular temperature, this is a very specific temperature of 2.17 Kelvin which is over here, so if I go on cooling this liquid further in this direction, let us say, a new liquid phase - liquid helium 2, emerges out. This is something different from what you see as compared to all other cryogenics. So, here liquid helium 2 emerges out, and therefore, what I call these 2 phases is as liquid helium 1, and liquid helium 2, or helium 1 and helium 2.

So, I just pointed out to you in earlier slide, that you have got different versions of putting helium in; that is, helium 3 and helium 4, which are nothing but isotopes. Again I am putting something, which is helium 1 and helium 2. Actually, this is liquid helium 1, and liquid helium 2, but in a colloquial language, I will always say - helium 1 and helium 2. So, what is helium 2? Helium 2 is a phase of liquid helium, which comes into existence when you go on cooling helium 1, and this new phase emerges when you go below 2.17 Kelvin, which is a very specific temperature. So, what is all this that we are talking about? The 2 different liquids now are called as, liquid helium 1, and liquid helium 2. So, this is clear from this diagram.

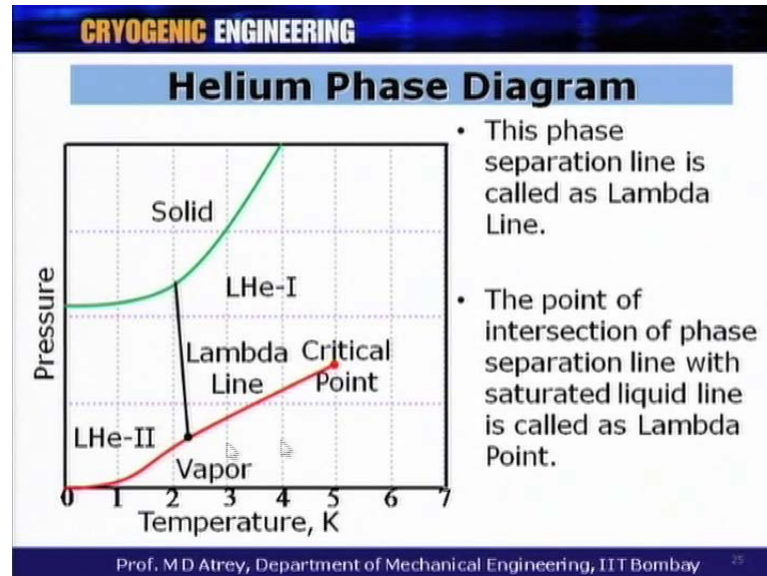
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Now, these liquid phases are distinguished on the basis of viscosity. So, I got some viscosity associated with helium 1, and I got some viscosity associated with helium 2; and on the basis of that I am doing this differentiation. Normally, liquid helium 1 is called as 'normal fluid', and helium 2 is called as 'super fluid'. Possibly, you must have

heard about this, that helium exists in 2 fluid forms - 1 is the normal fluid, and 1 is the super fluid form.

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What is this super fluid form? This is what you see from this. What I am giving you here is a line, which is joining 2.17 Kelvin up to this point, which divides helium 1, and helium 2.

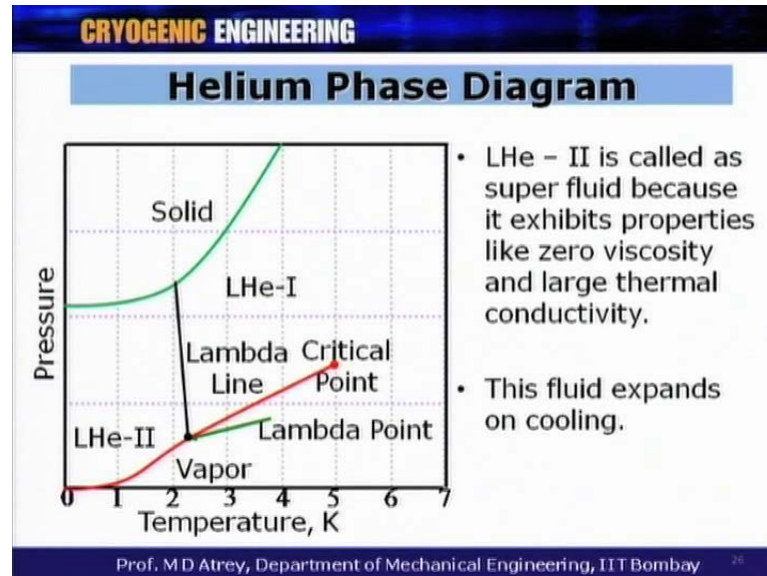
This phase separation line is called as 'lambda line'. So, imagine this is a 2.17 Kelvin touching up to this solid liquid line at this point, and this is what I call as 'lambda line', and this point is called as 'lambda point'. So, the point of intersection of phase separation line with saturation line, the intersection of phase separation line which is this, and where it hits the saturated line at this point, is what we call as a 'lambda point'. So, this is the lambda point.

Now, this is the complete phase diagram of helium, and I again I will summarize. What you have on the right side of this dividing line is helium 1; what you have on the left side of this line, is helium 2. Liquid helium 1 is called as 'normal fluid', and liquid helium 2 is called as 'super fluid'. The difference happens, as we go on cooling liquid helium 1 below 2.17 Kelvin, depending on what pressure you have.

The line which divides these two - helium 1 and helium 2, is what we call as 'lambda line', and the point where this intersects the saturated vapor line is the 'lambda point'.

This is very important to understand, and this is very important that a cryogenic engineer, who is expected to draw this diagram immediately, to understand this.

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Liquid helium 2 is called as 'super fluid' because, it exhibits properties like, 0 viscosity. We made a statement earlier that, this difference of helium 1 and helium 2, is owing to the viscosity of the liquids. This new phase, which emerges as helium 2 from helium 1, is basically because of viscosity differences between the 2 fluids.

So, helium 2 is called super fluid because, it exhibits properties like 0 viscosity. What I am talking about is helium 2 has got very close to 0 viscosity, while helium 1 like a normal fluid has got its own viscosity. What does it mean? It will never have effect like pressure drop, or friction. It can move in any direction. It is like mercury basically, and it can run in any direction. It can run for small little channels, you do not have to be really bothered about the pressure drops that are happening in helium 2. This is very important.

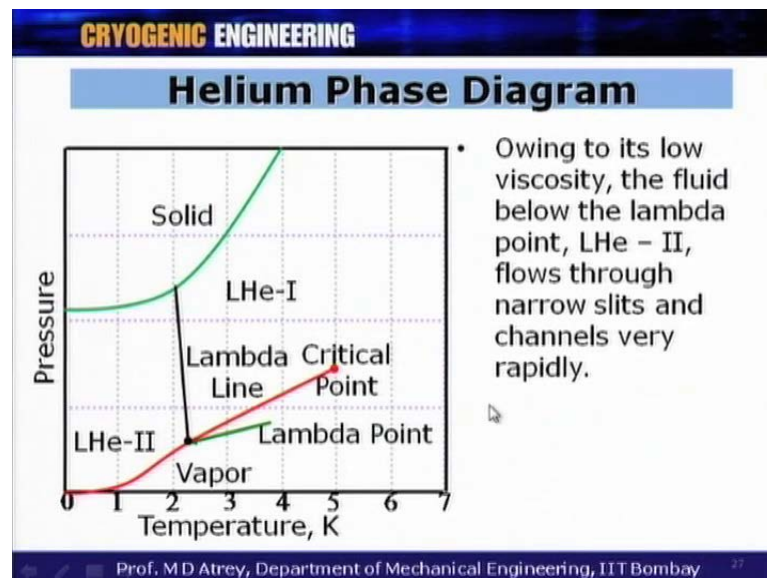
The other aspect of this is that, it has a very large thermal conductivity. Now these 2 aspects make the very important features of helium 2. Low viscosity, or 0 viscosity, or we also call as 0 entropy, as you come down to 0 Kelvin, it has become much more order. So, the most ordered thing is solid; you have got all the latest crystallized structures, you have got a very defined position, while in helium what you have got is as liquid helium is helium 2, which is becoming a very ordered liquid. It is not solid

exactly, but it is as ordered as solid. Therefore, what we call it as is '0 entropy' in this case.

So, it has got 0 viscosity, and it has got a very large thermal conductivity. Now, these 2 aspects are very important of helium 2. In addition to that, it has got very funny properties. See, a lot of researches are being done on helium 2, to understand the behavior of helium 2, this is called as 'super fluid'; because of its very high thermal conductivity, and because of its 0 viscosity, it has got different applications.

It ensures that, all the superconducting accelerators have got magnets, for example, in ((sar)), all the magnets are cooled at 1.8 Kelvin. 1.8 Kelvin is nothing but super fluid. What does it ensure? It ensures fantastic heat transfer; because, it has got a very large thermal conductivity, at the same time it has got 0 viscosity. So, whatever cracks are there, whatever ways are there, whatever paths are there, helium 2 will go and occupy the place; it will not worry about the pressure drops happening over there, because of absolute minimum or 0 viscosity. The other property is - this fluid expands on cooling, which is a very funny property. It cannot be well defined, but it is a pretty funny property of helium 2.

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Owing to its low viscosity, the fluid below the lambda point, that is liquid helium 2, flows through narrow slits and channels very, very rapidly. This is a very important aspect of helium 2 that, it can really flow through very narrow slits and channels, and

within no time. Otherwise you have to do pumping, and something like that. If we have got a mixture of helium 1 and helium 2, helium 2 of this mixture will immediately go through a slit or a channel, but helium 1 will not be able to go through. We will find lot of application of these in the next lecture, because we have got very specific experiments one can do on helium 1 and helium 2; because of this property of 0 viscosity, helium 2 can flow through narrow slits and channels very, very rapidly.

What happens when one goes from helium 1 to helium 2? What actually happens is, there is some kind of a phase transformation, which is called as a 'phase transition'. Although, one can see that it is only liquid on either side. So, in reality in reality there is no phase transition; that means there is a liquid to liquid phase transition. So, it is a completely different kind of phase transition in this case. One has to understand what the physics is behind this.

Till now, what we have understood is what the helium phase diagram looks like. We also concluded from here that, solid, liquid, and vapor never touch, or never coexist; and also that, when we cool liquid helium, it has got one more transition happening below the lambda point temperature, which is 2.17 Kelvin, and a new phase emerges called 'helium 2'.

Now, what I am going to talk about is, what this transformation or transition of helium 1 and helium 2 is all about. Let us see that in small details. Again the physics behind this is very, very big, and I am not going to discuss that. What I am going to discuss is only some important aspects of this phase transition.

Now, when I talk about phase transition, we have got a first order phase transition, and we have got a second order of phase transition also. This is the equation, which talks about Gibbs free energy. In thermodynamics, for any reaction, what you have is a Gibbs free energy equal to, we have got some internal energy E , we have got PV - pressure and volume variations here; then we have got a TS . So, G is equal to E plus PV minus TS . This is a very standard equation, which comes from Gibbs free energy equation.

Now, if I differentiate this Gibbs free energy, with respect to pressure, and if I take the first order derivative of this, at constant temperature it will give the density. So, if I see the variation of Gibbs free energy with respect to pressure at constant temperature, and constant mass, that means, whenever there is the phase transition happening at constant

temperature, and at constant mass, what you get is the density. This is the first order derivative of Gibbs free energy with respect to pressure at constant temperature, it gives density.

This density, which is the first order derivative of the Gibbs free energy, undergoes an abrupt change leading to discontinuity. So, whenever this kind of phase transition happens of first order nature, this is the first order derivative of Gibbs free energy, whenever this happens the density undergoes an abrupt change leading to a discontinuity, it is called 'Gibbs first order discontinuity' or 'first order transition'.

I am basically going to explain to you, what the first order transition, and what the second order transition is. In this case, which is a first order transition, what you see is, whenever the transitions of this nature happens, this happens at constant temperature, and the density goes through an abrupt change; that means, if I see the right side density, and the left side density, I will get a big discontinuity at a point where this transformation happens at a temperature, where this transformation happens. The density undergoes an abrupt change, leading to a discontinuity called the 'Gibbs first order discontinuity' or this transformation is called as 'first order transition' in this case.

What are the features of this transition? This transition involves latent heat. So, whenever a phase transition of first order happens, it happens it involves energy; either the energy is taken in, or the energy is given out.

The temperature of the system however, remains constant. What I am pointing at is, such a transition of first order is nothing but from gas to liquid, or from solid to liquid. So, whenever you see a conversion from liquid to gas, what has gone into it? It is latent heat of conversion. The temperature remains constant, latent heat gets involved, and the density changes abruptly. If I see liquid to gas conversion, there is an involvement of latent heat, and there is an abrupt increase in density when I go from gas to liquid, or the reverse will happen when I go from liquid to gas. This is what is called as the 'first order transition', where the phase changes from solid to liquid, or from liquid to gas, or from gas to liquid, and from liquid to solid. This is what I am going to talk about. For example, the first order transition is nothing but solid to liquid, or liquid to gaseous transition, the latent heat is absorbed at constant temperature. These are the features that are involved in the first order transition.

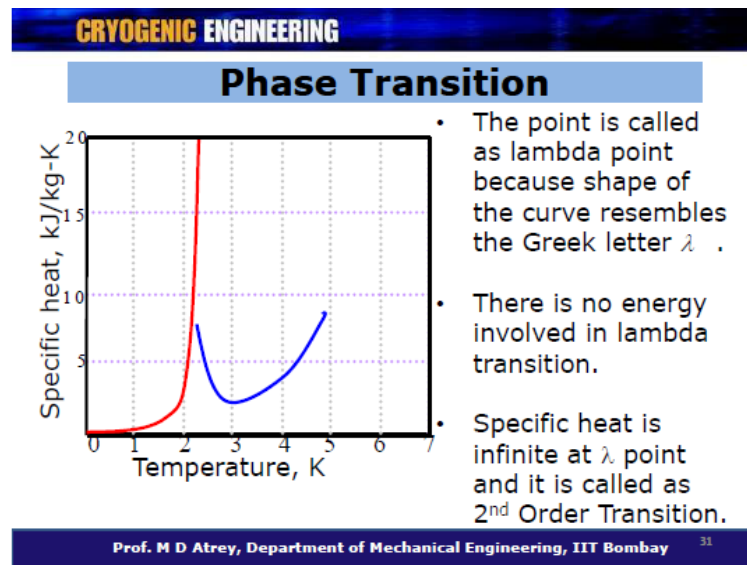
Now, we will see what the second order transition is. This is what happens when you get transformation from helium 1 to helium 2. These transitions are continuous in the first order form; but, exhibit discontinuity in the second order form. So, if I differentiate second time now, Gibbs free energy function, if I differentiate with respect to some other parameter 2 times, then I will get discontinuity there; and that is why this is called as 'second order phase transition'.

So, the second order derivative of Gibbs free energy with respect to chemical potential, because the chemical reaction is happening. Some kind of reaction is happening, and the chemical potential associated with that transition, if I differentiate Gibbs free energy, the equation of which I had given earlier, what I will get is the second derivative of this energy, which is nothing but specific heat.

In the first derivative what I had got was density; in the second order phase transition what I get is specific heat, and this variation of specific heat in liquid helium is an abrupt change in this case, and possesses a discontinuity at the lambda point. So, what we see in helium 1 and helium 2 is, the specific change drastically because, it is the second order phase transition.

In the first order phase transition what we had was density variation. In the second order derivation, second order phase transition, what we have is specific heat changes, or it is the discontinuity at the lambda point temperature, which is 2.17 Kelvin, and you will see what happens.

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So, this figure really gives you what exactly happens at lambda point. You can see that, on the y axis what I have plotted is the specific heat, on the x axis what you have is the temperature, and you can see here that, the specific heat variation is suddenly random at this point, and later this is an infinite kind of thing. So, there is a big change in specific heat capacity at a temperature of lambda point, which is 2.17 Kelvin. What can you conclude from the shape of this line? This point is called as 'lambda point', and why? It is because of the shape of this curve at 2.17; this looks like the geek letter 'lambda'.

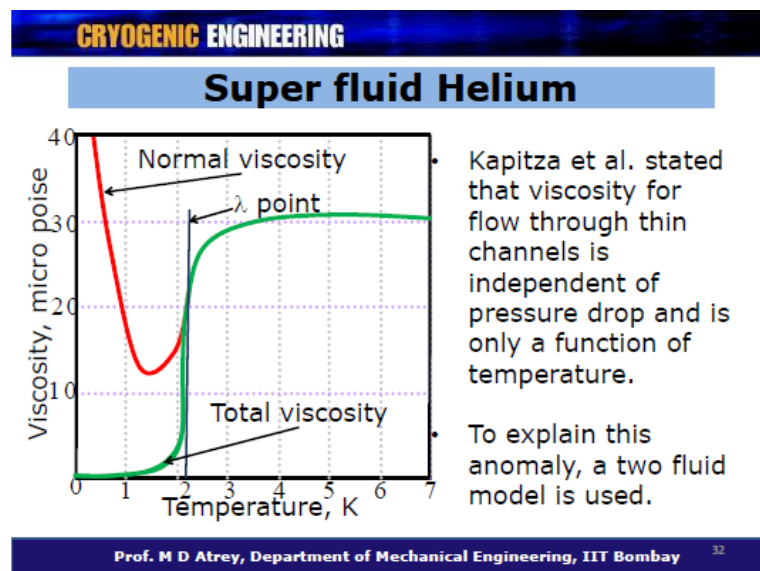
The geek letter 'lambda' denotes the specific heat variation at the lambda point, where the second order derivative of the Gibbs free function is discontinuous, and this is what is the discontinuity we are talking about at the lambda point; and this is why it is called as 'lambda transition' sometimes. There is no energy involved in lambda transition.

As I said in earlier case, first order transition, what you had was a latent heat conversion. We had a gas to liquid conversion, we had liquid to solid conversion or solid to liquid, or liquid to gas, where latent heat is given in or latent heat is taken out. So, an addition of heat, or removal of heat was involved. In this case there is no energy involved; there is a smooth transition from one phase, or one condition, to another condition. Liquid helium 1, to helium 2 what changes at this point is the abrupt change in the specific heat capacity at this lambda point; but, there is no energy involved in this lambda transition. These are nothing, but the characteristics of the second order phase transition, which is what is involved in the helium 1, to helium 2 transition.

The specific heat is infinite at the lambda point, almost infinite at lambda point; and it is called as 'second order transition'. So, one can call it as 'lambda transition', as far as, helium specific heat is concerned, or we can always called it as 'second order transition' in this case.

So, what we saw just now was - what is the first order transition, and what is the second order transition; and what we have to understand is, in the first order transition, density changes happen; in the second order transition, C P or specific heat abrupt changes are happening. This is what is very specific of helium. If you have understood that, we will go to the next part to understand what super fluid helium is.

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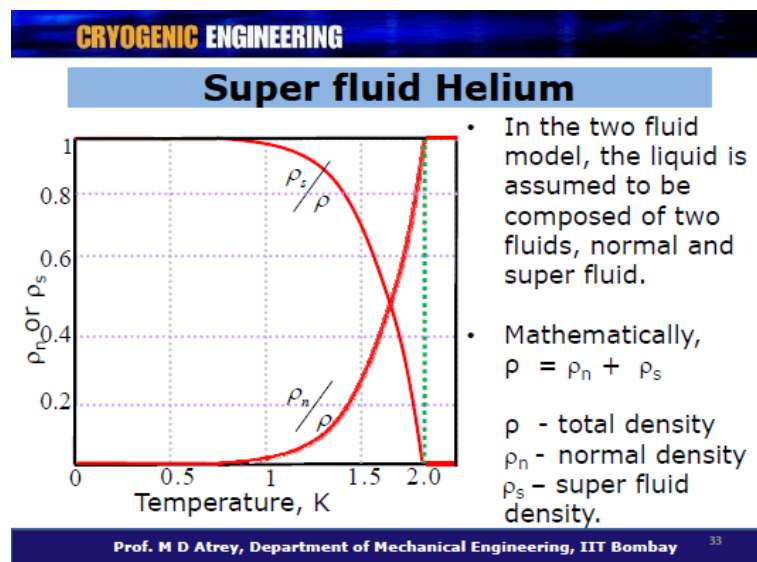
So, this curve is basically giving you - viscosity versus temperature. As I talked to you earlier, the helium 1 to helium 2 phase change, the helium 1 to helium 2 phase transition is basically because there is some viscosity change also. In addition to viscosity what has changed was this discontinuity, which happened of c p at lambda point; but how do I differentiate between helium 1 and helium 2 is basically because of its own viscosity.

Now, here you can see the viscosity, and how it changes for helium 1 and helium 2 on the right side of the lambda point, or the left side of the lambda point. Kapitza was a person who did a lot of work on helium, low temperature physics, and specifically on the helium 1 to helium 2 transitions. So, Kapitza stated that, viscosity for flow through thin channels is independent of pressure drop, and is only a function of temperature.

So, here you can see that viscosity is absolutely constant, as far as, normal helium is concerned; but as soon as you got a super fluid, so we got a normal viscosity associated with it, as soon as you came down below lambda point, the total viscosity decreases drastically. This is what you can see from this figure.

How to understand this? This has to be understood that, you had very high viscosity up to lambda point, and suddenly below the lambda point, the viscosity had changed; that means, you had different things happening below this. What is this? To explain this, normally, a two-fluid model will be used.

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What is this two-fluid model? Here I have got a different behavior below the lambda point. This is my lambda point temperature – 2.17 Kelvin, and below 2.17 Kelvin, I have got two curves, which are giving me the density variations in the super fluid, and the normal fluid.

In the two-fluid model, which was proposed by Kapitza, the liquid is assumed to be composed of two fluids, that is, the normal fluid, and the super fluid. So, on the left side of lambda point, what you have got is some normal fluid, and some super fluid.

As you go on reducing the temperature, at 0 Kelvin what you get is only the super fluid. As you go up to the lambda point, what you get is only the normal fluid; that means, what you have in between the lambda point, and 0 Kelvin is a mixture of normal fluid and super fluid. This is what a two-fluid model suggests, that the fluid between the

temperatures of lambda point, and 0 Kelvin has some density contribution coming from the super fluid, and some density contribution coming from the normal fluid. This is what a two-fluid theory is all about. Mathematically, I can write that, density at any point below 2.17 Kelvin is $\rho = \rho_n + \rho_s$, where ρ is the total density and ρ_n is the normal density, and ρ_s is the super fluid density.

So, the total density at any point below 2.17 Kelvin is a contribution from the normal density; that means, from the normal helium, and from the super fluid helium, or the density component coming from the super fluid.

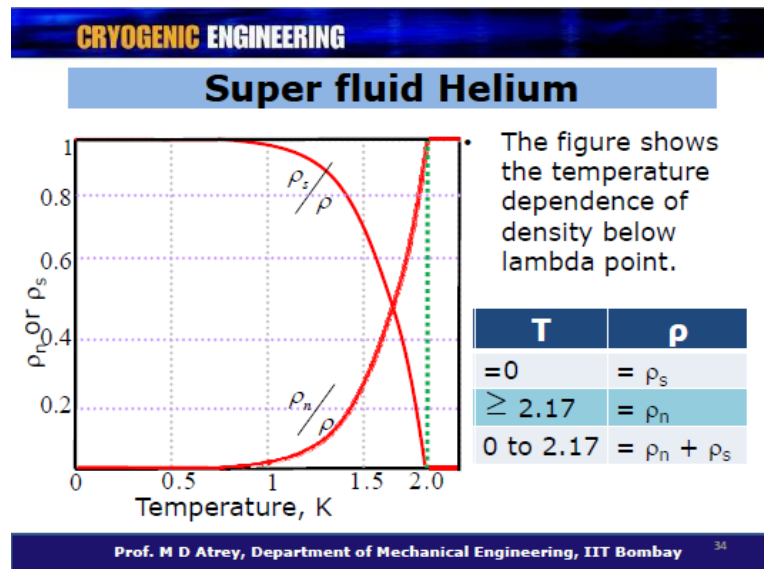
So, at any temperature below 2.17 Kelvin, what you have is a contribution coming from normal fluid, and contribution coming from super fluid. What you can see from this figure is, as you go below 2.17 Kelvin, ρ_n / ρ , is a ρ_n by total density. The density of normal fluid divided by total density is becoming absolute 0, which means that, the contribution of ρ_n is becoming absolute 0. It is coming to 0, while the ρ_s / ρ starts increasing below 2.17 Kelvin, and it almost becomes equal to 1, which means that ρ_s is equal to ρ_n , in this case.

Same thing is being given over here, at less than the temperature of 2.17 Kelvin, the contribution as you go down from 2.17 Kelvin towards 0 Kelvin the contribution of ρ_s is going to increase given as per this line, while as you go on the right side the contribution of ρ_n will start increasing. At lambda point, what you got is 100% ρ_n , or ρ is equal to ρ_n at the lambda point.

The figure shows the temperature dependence of density below the lambda point. What you can see as temperature is equal to 0, you get a ρ is equal to ρ_s ; that means, it is a hundred percent contribution of the super fluid in this case.

At a temperature more than or equal to 2.17, what you have is ρ_n , and between the temperature 0 to 2.17 Kelvin, you have got the component coming from the normal fluid and coming from the super fluid. So, ρ in this case equal to $\rho_n + \rho_s$.

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This is the two-fluid model, which explains to you, the total fluid viscosity safely compared to what we see in the viscosity, the super fluid component goes on increasing below 2.17 Kelvin, and therefore, the total viscosity almost reaches 0, at 0 Kelvin. While at lambda point you have got all the components in the normal helium, and therefore, rho n contributes to that, and therefore, the normal viscosity will come into picture.

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CRYOGENIC ENGINEERING

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 $T < \lambda$ point temperature, the apparent boiling of the fluid stops.

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If you talk about heat transfer, we just talked about viscosity, the heat transfer in super fluid helium, that is, liquid helium 2 is very, very special. When the pressure above

liquid helium 1 is reduced by pumping, the fluid boils vigorously. So, if I remove the pressure, the boiling of liquid helium 2 will; when the pressure above liquid helium 1 is reduced by pumping the fluid boils vigorously.

During pumping, the temperature of the liquid starts decreasing. So, I have got some liquid helium 1, and I remove the pressure over it, what will happen? The temperature of the liquid will decrease, and a part of the liquid gets boiled away; but, as soon as temperature of the liquid reaches less than lambda point temperature, that means, less than 2.17 Kelvin, the apparent boiling of the fluid stops; that means, what was vigorously boiling earlier, which you could see from outside, suddenly will come to stand still, and a very quiet and apparent boiling, which you could see from outside will stop suddenly, which is happening at T less than lambda point temperature. Why does it happen?

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CRYOGENIC ENGINEERING

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} |

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The liquid now, at a temperature less than lambda point temperature, it becomes very clear and quiet even though it is vaporizing rapidly. So, vaporization is happening, the boiling is happening; however, it has become very clear and quiet, and not vigorous as it was when the temperature was above the lambda point. This difference in boiling is as soon as the liquid comes below the lambda point. Why? It happens because, the thermal conductivity of liquid helium 2 is very, very 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.

Now, this is the real reason as to what happens below the lambda point temperature. Below the lambda point temperature, the viscosity of helium 2 is so large that, before the bubbles reach the surface, which is what happens in normal boiling, the heat is getting conducted because of the very high conductivity of helium 2. Therefore, because the bubbles do not rise up, that vigorous boiling stops, liquid apparently looks very quiet and clear, and that is why the word which we had use earlier that, apparent boiling phenomenon stops. You cannot see boiling happening over there, but boiling is happening.

You can see from this table, how the thermal conductivity changes. If one goes from helium 1 to helium 2, you can see here that helium has got a thermal conductivity at point 0, 2, 4 watt per meter Kelvin, while helium 2 has got 6,500 watts per meter Kelvin thermal conductivity. So, you can see relative difference between these two conductivities easily, and can understand why that apparent boiling, which I talked about stops as soon as helium 1 goes to helium 2 state below lambda point temperature.

Similarly, you can see what happens to the viscosity, which is in minus 10 to the power minus 6, right in this region, while it has gone to the 10 to the power minus 7, to minus 12, depending on the slit size the viscosity will now show changes. The viscosity will be different for a bulk flow, and for flow in small pipes, and small slits. These two property changes of thermal conductivity, and viscosity, make helium 1 and helium 2, as two different fluids, two completely different fluids, and therefore, their utilities also could be different because, of these changes in properties. So, this is what we talked about of helium 1 and helium 2, and also about the phase transition.

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CRYOGENIC ENGINEERING

Information

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

Just additional information I want to add to this lecture is that, Kapitza of whom we talked about, was awarded the Nobel Prize in Physics, in the year 1978, for his basic inventions and discoveries in the area of low temperature physics. This is what we talked about and his contributions to the super fluidity of the helium.

This is my end of this lecture; and what you have here is a self assessment exercise. It is given after this slide; again, please kindly assess yourself very honestly. This will give you feedback about this lecture. These are the different questions over here, which you are expected to answer yourself. I have given the answers also at the end of this.

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CRYOGENIC ENGINEERING

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 _____

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CRYOGENIC ENGINEERING

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.

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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.