Thermal Physics
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Lecture - 60
3rd Law of Thermodynamics

Hello and welcome back to the last lecture of this NPTEL lecture series on thermal physics. Now this week we have, so far we have discussed about black body radiation and we have seen that keeping in mind the similarity between black body radiation and an ideal gas, gas assembly, if we decide to treat black body radiation as a thermodynamic system, we can get quantities like entropy.

We can derive or we can you know describe an isothermal and adiabatic process in a cavity radiation. We can also calculate, compute all the free energy or energy functions and last but not the least, we can also derive or we can also discuss a phase transition in a cavity radiation.

Now one aspect of cavity radiation that I have omitted and I initially I thought it is not very important because we are not going into the details anyway, but then I thought okay, so better to give a very short perspective on that. And that is the black body radiation of or the Planck's law of black body radiation. Now what is Planck's law?

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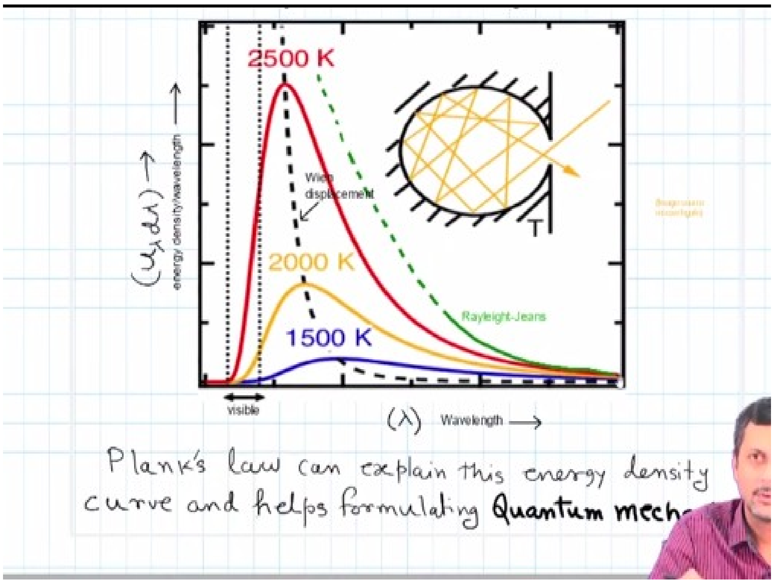

Plank's law can explain this energy density curve and helps formulating Quantum mech

If we look into it, if we look into the energy density as a function of wavelength or frequency, both ways it will look the same, the plot looks something like this. Now this is these are not strictly speaking these are not the experimental plots. These are also you know theoretical simulation, but let me tell you the, I mean the matching between the, you know matching between theory and the or experiment and the theory that was derived by Planck is pretty remarkable.

So initially, so let us assume for now that this red one for example is a, what you call the experimental data, which is which it is not. But so initial attempt was to and by the way, what is cavity radiation, I mean where to measure this energy density? It is not along the body of the black I mean along the surface of the black body because black body are typically made the surface are made reflective.

And what is a poor absorber is also called emitter. So we have to concentrate on the radiation that comes out of this opening, tiny opening of the black body. Now initial, the early attempt in order to explain the shape of this black body, black body radiation curve, was given by Rayleigh and Jeans.

So they had a semi I mean classical approach that is to say so that and they could explain the long wavelength behavior of black body pretty well, black body radiation pretty well. But it failed miserably towards the short wavelength range and this is what is called ultraviolet catastrophe. Then came Wien’s displacement law, which actually talks about the, you know the location of the maxima as a function of temperature.

So according to this law the product of the maximum temperature or the temperature of the cavity and the maximum of this distribution function is a constant. So if the temperature falls, because it is a constant, so the value, the maximum value should shift toward right, okay. So now this things it was you know individual I mean it was discrete attempts to explain the black body radiation.

But finally, when Planck came up with his rule or his laws of black body radiation, so basically he came up with the concept of quantized photon energy. Only then he could actually compute I mean actually work out a theory that can explain this curve with very good accuracy.

And it turns out that in certain limits, it can also give, I mean it can also give Rayleigh–Jeans law and Wien's displacement law also comes out of Planck's theory. Now this we have I have not discussed primarily because, this type the any discussion on quantum mechanics should start from this point. So this is primarily the old quantum theory and not much to do with the thermodynamics.

Some statistical mechanics definitely what Planck used in order to explain I mean get to his results, but primarily yeah some statistical mechanics and quantum theory. So that is why I have omitted this from our earlier discussion. Anyway, so I thought it is better to have a quick look at it.

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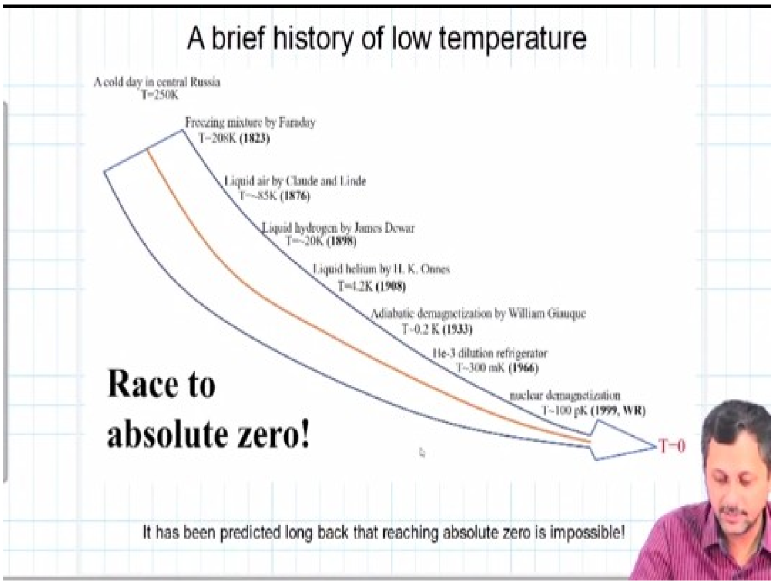

A brief history of low temperature

A cold day in central Russia
T=250K

Freezing mixture by Faraday
T~208K **(1823)**

Liquid air by Claude and Linde
T~-85K **(1876)**

Liquid hydrogen by James Dewar
T=~20K **(1898)**

Liquid helium by H. K. Onnes
T=4.2K **(1908)**

Adiabatic demagnetization by William Giauque
T~0.2 K **(1933)**

He-3 dilution refrigerator
T~300 mK **(1966)**

nuclear demagnetization
T~100 pK **(1999, WR)**

T~0

Race to absolute zero!

It has been predicted long back that reaching absolute zero is impossible!

Now apart from this the last topic, which we are going to cover today is the topic of you know low temperature physics and third law of thermodynamics. Now what is third law of thermodynamics, that we will come, we will come back to that. But before that, let me give you a very brief history of low temperature or we can also call it the rest to absolute zero.

So here in this at the end of this arrow, we have T is equal to 0, which is the absolute zero temperature. So all the temperatures are in Kelvin by the way. So this is the absolute zero temperature. And let us quickly look into the progression with time with in the modern history towards this absolute zero.

Now snow or ice or whatever you might call it, the temperature of that, the maximum temperature that we can have in a snowy day is somewhere around 0 degree centigrade, may be slightly higher, maybe slightly lower, I mean could be lower than 0, but around 0 degree centigrade. But even in a in the cold country, for example Central Europe, Russia, some parts of US, also in India the Himalayas, the temperature can go much lower than that.

Now typically, a cold day in Central Russia or you know in the peak of some tall Himalayan mountain, we can have the temperature might go down to -20 or sometimes even -30 degree centigrade. So let us say we have T is equal to 250 Kelvin. Now that is naturally occurring. So why I gave 250 Kelvin? So this is probably the average low temperature that occurs naturally in, that occurs naturally.

Of course we have a record low I guess, record low is somewhere around minus 45 degree centigrade, but that is only a special case. So we are not going into that. Now 1823 Faraday uses and historically speaking human used to I mean people used to mix different salts with ice in order to produce ice cream and other cold food items.

So people knew that mixing of salt with ice reduces the temperature further below the freezing point of ice or melting point of ice. Now Faraday used a similar technique. He used, he could reach all the way down to 208 Kelvin, using a freezing mixture so that he could liquefy ammonia. That is 1823. 1876, then the okay, it is only a very brief history.

So there has been lots of development in between times. And you know between 1823 and 1876, the laws of thermodynamics took its shape, especially the second law took its shape. People could understand the working principle of refrigerators, working principle of engines. So when Linde came up, what Claude and Linde did was actually they mechanized the procedure of liquefying gases.

It is not only a freezing mixture anymore, but there are certain mechanized compressor parts and they could liquefy air at around -85 Kelvin. Now at liquid air temperature is kind of midway between liquid nitrogen and liquid oxygen temperature to yeah these two values. So it is approximately minus sorry 85 Kelvin. It took another 20 years, it took another 20 years to go down to liquid hydrogen temperature.

That was developed by James Dewar in 1898 and another 10 years to liquid helium temperature by Onnes in 1908. So liquid helium temperature is 4.2 Kelvin and very soon it was discovered that if we pump on a liquid, now we have learned phase transition and we have learned if we reduce the pressure on a liquid, then it will start boiling at a much lower temperature, right?

So that we have seen, we have done problems and the opposite is also true. If we pressurize the liquid, it will boil at a higher temperature. So immediately it was discovered that if we if people start pumping on liquid helium the temperature can go down even to 1.2 Kelvin, that is also possible, right?

Then the, but again if the barrier was approximately 1 Kelvin, people could not go below 1 Kelvin and another like 25 years till William Giauque and other scientists they came up first initially the concept was given in 1927. Then experimentally it was described in 1933 the process called adiabatic demagnetization. So the concept is the following.

We have magnetic salt, paramagnetic salt, which is exposed to a very strong magnetic field and suddenly and it is already at low temperature approximately around 1 Kelvin or so that is cooled by liquid helium. And suddenly the magnetic field is withdrawn. So then what happens, it is equivalent to an adiabatic expansion of the system. So the magnetic ordering, the magnetic dipoles were already pointing towards the magnetic field.

Now when the magnetic field is withdrawn, they will be fanning out, they will be randomly distributed in all directions in the cost of internal energy. And the process will, this adiabatic demagnetization will reduce the temperature further. And it was found out that it can go down to 0.2 Kelvin. Another 33 years till the helium-3 dilution refrigerator was first invented in 1966.

I should not call it it was first invented, but using that refrigerator around 1966 it was possible to achieve a low temperature as low as 300 milli-Kelvin, okay. So that is pretty low and but it did not stop there. Another 33 years a nuclear demagnetization method was used on a rhodium metal and it could be cooled all the way down to 100 pico-Kelvin which still is the world record of a lowest, for a lowest temperature of an object.

Of course, afterwards like that is already like 23 years, okay. So in last 23 years, there has been many experiments, many attempts to reach even closer to absolute zero. People could go I mean there are occasions where one or two atoms or maybe a small group of atoms could be taken to a temperature close to 10 pico-Kelvin or so.

But those are you know we cannot really call it a you know cooperative cooling because that happened only on a very tiny cluster of you know local cooling I would say, tiny cluster of molecules. So till now 100 pico-Kelvin is the lowest achievable temperature on a finite size object, right. So that means although we are very close, scientists are very close to absolute zero, we are still very far.

Like in the scale you see, up to this point the scale was going down in you know 10s of degrees. So you know from here to here, there is the order of magnitude. And after this 4.2 Kelvin mark, then immediately after that there is a one like 1 Kelvin is also around this time. After that it went down to 0.2 Kelvin in like 12 to 25 years. Next 33 years it went down by another two orders of magnitude.

And next 33 years it has all went down by another two orders of, sorry not two it is more than, milli to pico. So it is, oh it is huge. So minus 3 to minus 12. So nine orders of magnitude. But this absolute zero is still far, yet we are very close. That, I mean now we you know the intuition worked a long time, I mean long time before this temperature was even thought of, right?

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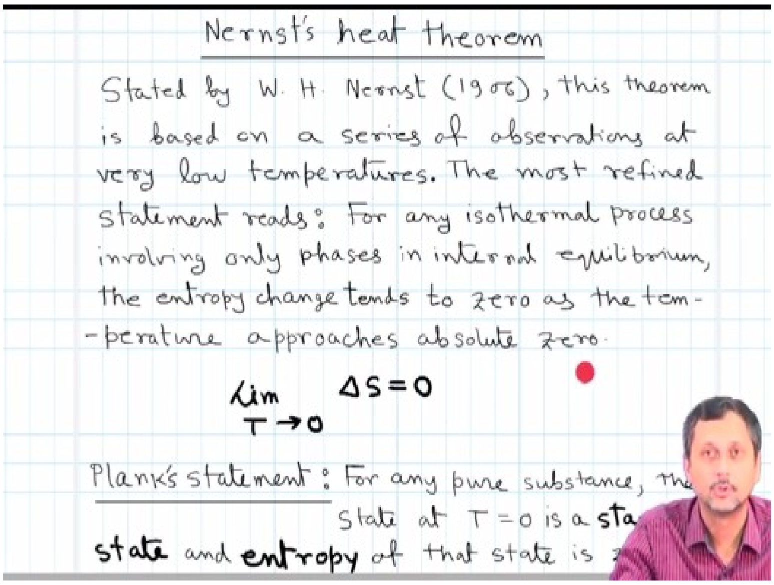

Nernst's heat theorem

Stated by W. H. Nernst (1906), this theorem is based on a series of observations at very low temperatures. The most refined statement reads: For any isothermal process involving only phases in internal equilibrium, the entropy change tends to zero as the temperature approaches absolute zero.

$$\lim_{T \to 0} \Delta S = 0$$

Plank's statement: For any pure substance, th

State at $T = 0$ is a sta

state and entropy of that state is

So it was 1906 when the when scientist W. H Nernst was you know measuring the specific gravity or sorry the specific heat of series of chemical salts. He came up with the observation and he eventually came up with a theorem called the Nernst's heat theorem that says for any isothermal process, for any isothermal process involving only phases in internal equilibrium okay, the entropy change tends to zero as the temperature approaches absolute zero.

So this is a, so there are many different versions of this. This was definitely not the first version of this theorem or law, whatever you call it. So initially he gave some statement, later on it was found out some improvements is needed, there are scopes of improvement and the eventually the present form which or present acceptable form is for any isothermal process.

The entropy change goes towards zero as the temperature approaches absolute zero for the systems or only pure phases in an internal equilibrium, right. Now another few years down the line Planck modified the statement slightly and said for any pure substance the state at T equal to 0 is called, can be called a standard state. Standard state means, it does not matter how to how we reach there.

But once we reach there, it will be used as an universal reference, right? So he said that T equal to 0 is a standard state and the entropy of that state is 0. Please note the condition that for any pure substance. And it is understandable that any pure substance, I mean it could be what I mean to say by pure substance is, it is not an element, it is not necessarily an element.

But even if it is a compound, the compound is in its purest possible form. No defects, no impurities, nothing. And it is understandable that this low temperature only one possible state of matter exists that is the solid state. So that means what he meant to say is or what he said is there are other alternative version of this statement that says for a pure crystalline solid, the state at T equal to 0 is a standard state where entropy is zero okay.

So I purposefully you know did not use the word crystalline here, because there could be other systems also which are you know actually statistical mechanics also allows to observe you know or predict the entropy of other systems close to absolute zero. And the systems might not be you know solid, which we can think of. It could be a spin system, it could be an amorphous class.

So we will come to that. We will discuss that towards the end of this lecture. Anyway, so that was Planck's statement. And what does it mean?

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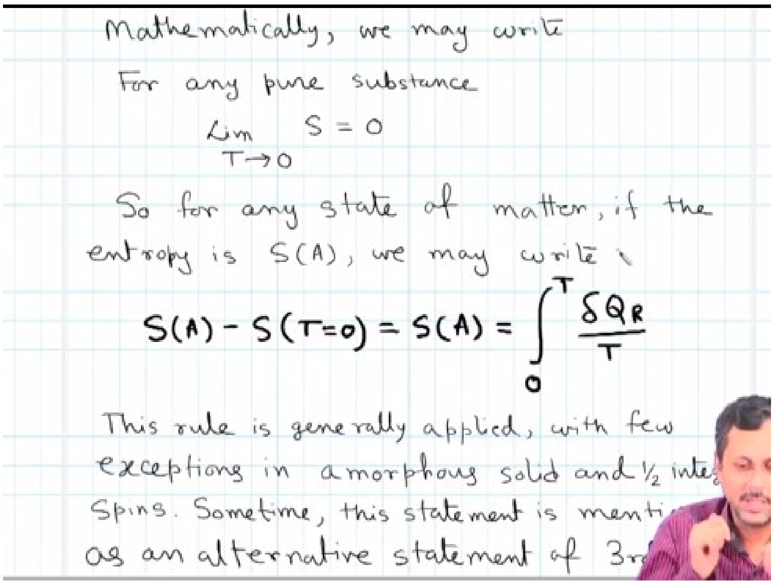

Mathematically, we may write

For any pure substance

$$\lim_{T\to 0} S = 0$$

So for any state of matter, if the entropy is S(A), we may write :

$$S(A) - S(T=0) = S(A) = \int_0^T \frac{\delta Q_R}{T}$$

This rule is generally applied, with few exceptions in amorphous solid and ½ inte

Spins. Sometime, this statement is menti

as an alternative statement of 3r

Mathematically, it means that limit T tends to 0 S is equal to 0 for any pure substance. Now there is a subtle difference between what Nernst says, and what Planck says. Nernst says that the delta S becomes 0 as T goes to 0. So that means the change in entropy. And Planck says, no it is not the change in entropy we are talking about, it is the absolute entropy, that goes to 0, of a pure state goes to 0 as we approach absolute zero, right.

Now this has even more I mean it is a far reaching implication, because for any state, let us denote this by A, so we can write the entropy, corresponding entropy as S bracket A. So S(A) and we know that entropy calculation is typically done on any reversible path. So that means the integration delta Q R, R means reversible, by T has to be evaluated along any reversible path.

And we can always compute the difference between the initial and the final state. So S(A) minus S(T=0), which is essentially why Planck's you know Planck's theorem, this is equal to 0. So that means, this is equal to S(A), this is equal to integration 0 to T delta Q R divided by delta Q R times T. So this means, this R stands here for reversible changes. Now this rule is generally applicable with few exceptions.

For example, in amorphous solids and in half integer spins and sometimes, this statement itself is mentioned as the statement of the third law. But it so happens that there is a much more general statement of Third Law, which, from which we can eventually, you know mathematically derive this particular statement.

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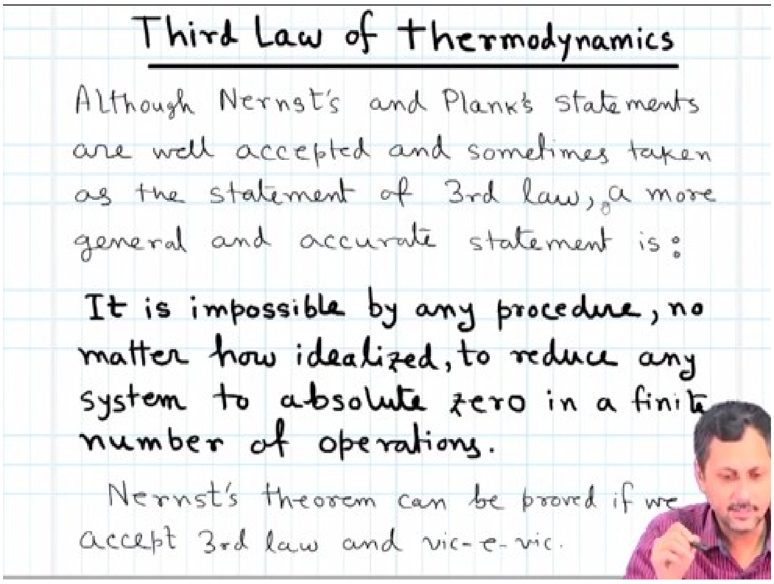

Third Law of thermodynamics

Although Nernst's and Plank's statements are well accepted and sometimes taken as the statement of 3rd law, a more general and accurate statement is:

It is impossible by any procedure, no matter how idealized, to reduce any system to absolute zero in a finit number of operations.

Nernst's theorem can be proved if we accept 3rd law and vic-e-vic.

And that is the third law third of, that statement is actually called the third law of thermodynamics. Please remember the statement I am going to tell you, in some of the books you will find the Nernst statement and Planck's statement is also mentioned as third law.

Now that is fine because you know it can be proved the equivalence of these laws can also be proved similar to the second law of thermodynamics where we have a Kelvin Planck statement and one we have a what was it, Clausius statement and the equivalence of those can be proved. Now what is the statement?

The statement is, it is impossible by any procedure no matter how idealized, to reduce any system to absolute zero in a finite number of operations. Now this is a very strong statement and once again like the first law and the second law, this statement cannot be proved, okay. So this statement has to be accepted so that we can prove the heat theorem.

And also there are ways of somehow show that if the heat theorem that means this particular statement is valid, then this also indicates to this particular you know statement. But I prefer to you know believe that this is a much more you know comprehensive form of the third law of thermodynamics.

And heat theorem given by Nernst or Planck is only a corollary of this particular statement, okay. Okay. So this is the one and once again we cannot prove it. We will not go into the details of how to show the equivalence or rather how to prove Nernst theorem from this particular statement. If you are interested you can look into any standard textbook and there are some discussion, certain discussion on this particular you know particular topic.

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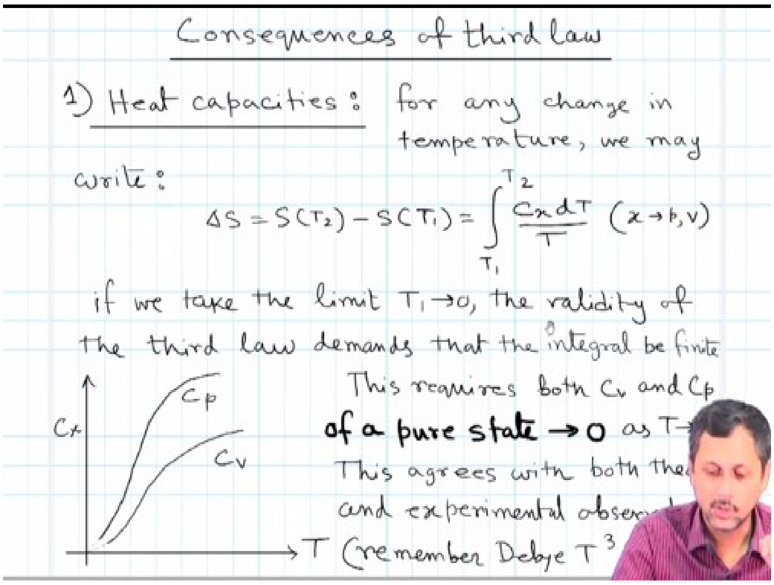

Consequences of third law

1) Heat capacities: for any change in temperature, we may write:

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_x\, dT}{T} \quad (x \to p, V)$$

if we take the limit $T_1 \to 0$, the validity of the third law demands that the integral be finite

This requires both C_v and C_p

of a pure state → 0 as T

This agrees with both the

and experimental obser

(remember Debye T^3

But what we are going to do is, for the remaining of this lecture, we will be talking about the consequences of this third law. Now what happens to the heat capacity? Delta S is equal to S of T2 minus S of T 1. That means integration T 1 to T 2 C x dT by T where C x is the heat capacity. Now x could be p or V or basically anything. I mean it is not necessarily that one, necessary that one process is either you know isobaric or isochoric.

It could be any other arbitrary process. It can be you know it can be performed along an allotrope or sorry polytrope or any other path. But in general we can for any process we can write a heat capacity C x, right? So x could be p or V or could be anything. But what is important here, now if we focus on the, you know integration, the mathematical expression for integration and set T 1 is equal to 0.

So that means, S of T 1 goes to 0 according to, so assuming that we have to okay so here we have to accept the I mean you know the what you call the equivalence between the third law of thermodynamics and you know and Planck's statement. So that means according to, we can say according to third law of thermodynamics S of T 1 is equal to 0 as T 1 tends to 0.

So that means, delta S will be simply equal to S of T 2 and for S of T 2 becomes finite, this integration will be 0 to T 2 some C x dT divided by T, okay. Now in the lower limit what happens? I mean if we integrate it and if we put the lower limit, then the integrand or rather even before integration if we just put the limits in the integrand, in the lower limit the integrand will divert.

So this integration cannot be performed. So from pure mathematical consideration given that S of T 2 has to be a finite quantity, we can say that as T 1 goes to 0 C x or the heat capacity also needs to go to 0 for any pure state, okay. Because please remember the Planck's statement is valid only for a pure state here, right?

So for any pure state as the temperature goes down both C p and C V, however they behave okay at higher temperatures, they must approach 0. And this is something that we have already seen. Remember the Debye theory of Debye T cube law from specific heat of solids, right? So we have seen that at very low temperature, the specific heat of a solid behaves as if it varies with t cube.

And as T goes to 0 T cube T cube also goes to 0. So we have already seen this is happening in practice, right.

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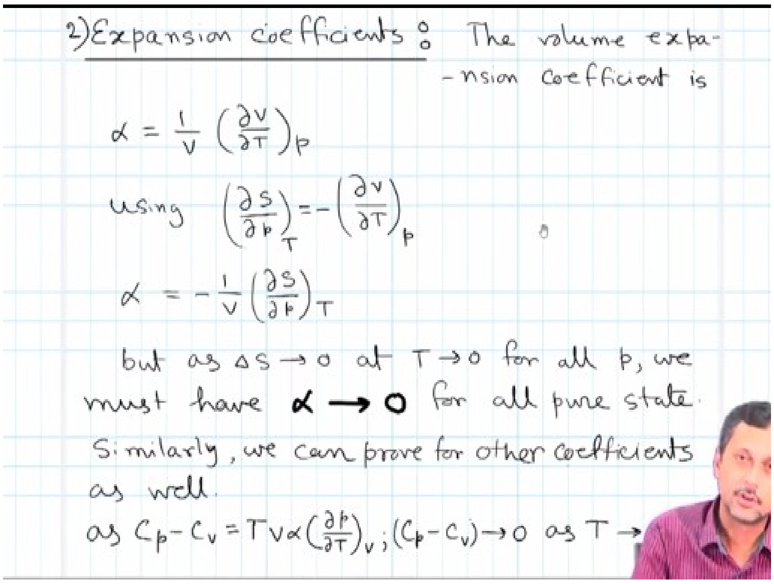

2) Expansion coefficients : The volume expansion coefficient is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

using $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$$\alpha = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T$$

but as $\Delta S \to 0$ at $T \to 0$ for all p, we must have $\alpha \to 0$ for all pure state.

Similarly, we can prove for other coefficients as well.

as $C_p - C_v = TV\alpha\left(\frac{\partial p}{\partial T}\right)_v$; $(C_p - C_v) \to 0$ as $T \to$

Now for the expansion coefficient, the volume expansion coefficient for example, this is alpha is equal to 1 over V del V del T p and we use the thermodynamic relation that S del p T is equal to minus del V del T p. We can write alpha is equal to minus 1 over V del S del p T. But as delta I mean when we go towards absolute zero the isothermal expansion coefficient, isothermal volume expansion coefficient also goes to 0 because, this is a change in entropy.

So delta S as T goes to 0 delta S also goes to 0. So we have alpha going to 0 for any pure phase. So and interestingly this is not only valid for pure phase but for any object because only for pure phase this is a absolute necessity. But, in general, if we accept the heat theorem by Nernst in its original form, then delta S going to 0 delta is equal to 0 as T tends to 0 for any substance.

So for any substance not only for pure systems, we have alpha goes to 0 as T goes to 0. And without surprise, as for any object C p minus C V is equal to T V alpha del p del T V, we can also write as alpha goes to 0 as T goes to 0 that C p minus C V goes to 0 as T goes to 0, which is also obvious from this. The difference between C p and C V diminishes as we approach towards low temperature.

And at T equal to 0, the difference should also be equal to 0. So that means, at C p and C V both should follow, I mean both should converge or confluence at one single point, okay. And the value should be equal to 0. So there is no heat capacity whatsoever at 0 temperature for any object, right.

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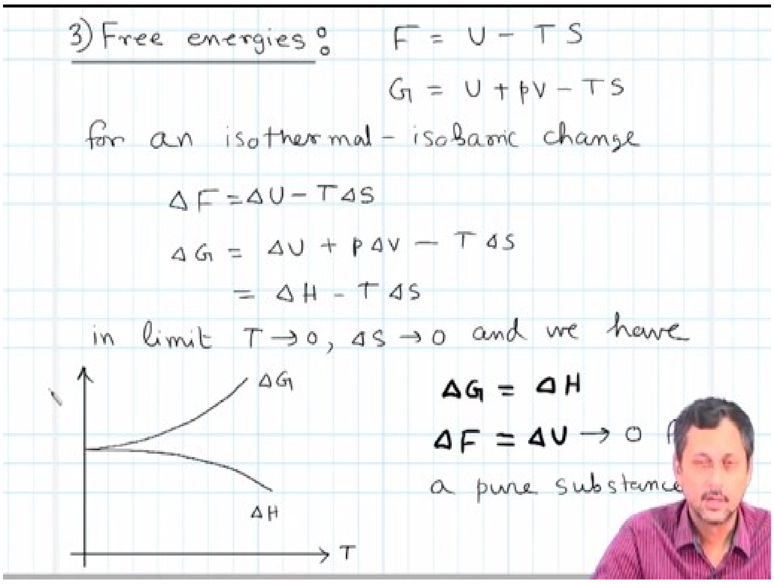

3) Free energies: $F = U - TS$

$G = U + pV - TS$

for an isothermal - isobaric change

$\Delta F = \Delta U - T\Delta S$

$\Delta G = \Delta U + p\Delta V - T\Delta S$

$= \Delta H - T\Delta S$

in limit $T \to 0$, $\Delta S \to 0$ and we have

$\Delta G = \Delta H$

$\Delta F = \Delta U \to 0$ f

a pure substance

Now what happens to the free energy, energy functions? Energy, I mean there are two free energy functions H F and G. We see F is equal to U minus TS and G is equal to U plus pV minus TS. Now for an isothermal isobaric change, if that means change occurring at constant temperature and constant pressure, we can write delta F is equal to delta U minus T delta S.

Delta G is equal to delta H minus T delta S where delta H is equal to delta U plus p delta V. Now in the limit as T goes to 0 delta S also goes to 0. Once again we do not have to have a pure system for this. For any system T goes to 0 delta S goes to 0. And we have delta G is equal to delta H and delta F is equal to delta U.

So that means, if we plot the two change in enthalpy and change in Gibbs free energy in the same plot, we should get a confluence I mean once again it will confluence to a single point as temperature goes to 0. What happens to delta F?

Delta will be equal to delta U and that should also go to 0 because as entropy approaches 0 at low temperature so the internal energy for at least for a pure system also should go to 0. Now what happens for impure system? Let us discuss that.

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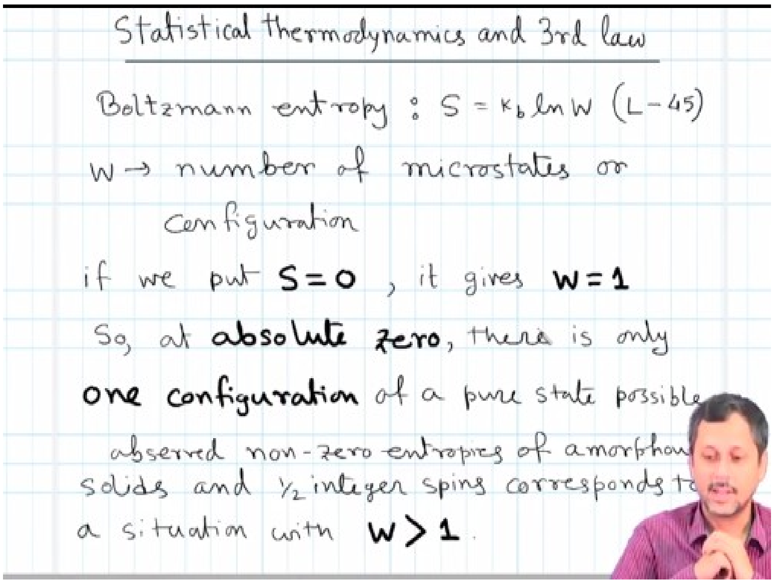

Statistical thermodynamics and 3rd law

Boltzmann entropy : $S = k_b \ln W$ (L-45)

$W \rightarrow$ number of microstates or configuration

if we put **$S=0$**, it gives **$W=1$**

So, at **absolute zero**, there is only **one configuration** of a pure state possibl

observed non-zero entropies of amorphou solids and ½ integer spins corresponds t a situation with **$W > 1$**.

Now according to statistical mechanics, you remember in lecture 45, we have given this relation without proving of course because this is the you know proof of this lies in the domain of statistical mechanics, which is beyond the scope of this lecture series. S is equal to K b ln W where K b is the Boltzmann constant, W is the number of microstates or configuration of the system in question.

Now if we put S is equal to 0, it gives W is equal to 1. So that means, at absolute zero there is only one configuration of a pure state possible. Then that makes very, I mean very much sense because, if we talk about a pure system at absolute zero what is that? A pure system is a perfect crystal without any defect, without any impurity in it.

I mean, it could be a compound, it need not be a, you know need not be an element, crystal of an element but it has to be pure and defect free. So in those case if we have even have 1 billion number of atoms or molecules present in that they has to be arranged, there is only one way they can be arranged so that there is a pure crystal present. So there is only one unique configuration.

Please remember that at T equal to 0 all the vibrations die, forget about rotation. So there is no movement of the molecules, no movement of this atoms or molecules whatever, and they are sitting exactly at the place they are supposed to be. So this is a perfect crystal with only one configuration possible and that is why we get W is equal to 1. But then what happens for in not so pure systems?

We can have systems, statistical mechanics, I mean from statistical mechanics it can be shown that there are systems where for example amorphous solids or half integer spin system, even at T equal to 0, they possess a good degree high degree of degeneracy. They can possess high degree of degeneracy so that W is greater than 1. That means S will not be equal to 0.

So for those type of systems, even the delta U will not be equal to 0. So delta F you know that relation delta F is equal to delta U at T equal to 0 is still valid, but for those non pure systems delta U will not tend to 0 value as the temperature goes to absolute zero, okay. So there will be some unrelaxed this one unrelaxed Gibbs free energy, sorry Helmholtz's free energy or some internal energy.

And also there will be some finite entropy for those types of systems. So this is not a violation of the third law I would say. But this is something that has to be learned, I mean that has to be understood only from the perspective of statistical mechanics, okay. So this actually concludes our discussion on thermal physics. And I do not want to summarize what we have learned in this last 12 weeks because this summary will itself take a long time.

But I, all I can hope that you have enjoyed the session as much as I did, enjoyed the discussion forum as much as I did. And you have, most importantly you have learned something from the course. That is all I can hope. And finally, I would like to say thank you to all of you and to the entire NPTEL team for their wonderful effort and wonderful effort and support. And also I want to thank you for your participation. Have a good time ahead and goodbye.