Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture – 17

Negative Temperature

Welcome back to the next lecture on Statistical Thermodynamics. We have talked about β, β is equal to 1 over kT, where T is temperature on absolute scale. Today we will talk about negative temperature. What is the meaning of negative temperature? Is negative temperature possible? So therefore, in order to discuss this, we will also revisit the third law of thermodynamics a little bit. Let us get started. We will begin with talking about Boltzmann distribution.

Remember that Boltzmann distribution or in other words fractional population of a state is given by n_i upon n is equal to exponential minus βE_i upon q. Similarly, let us choose another state n_j upon n is equal to exponential minus βE_j upon q. These are the expressions for the fractional population of i^{th} and j^{th} state for a system which has n number of molecules and the partition function is q. And if I now write the ratio n_j upon n_i, it will be equal to n and q and q will get cancelled.

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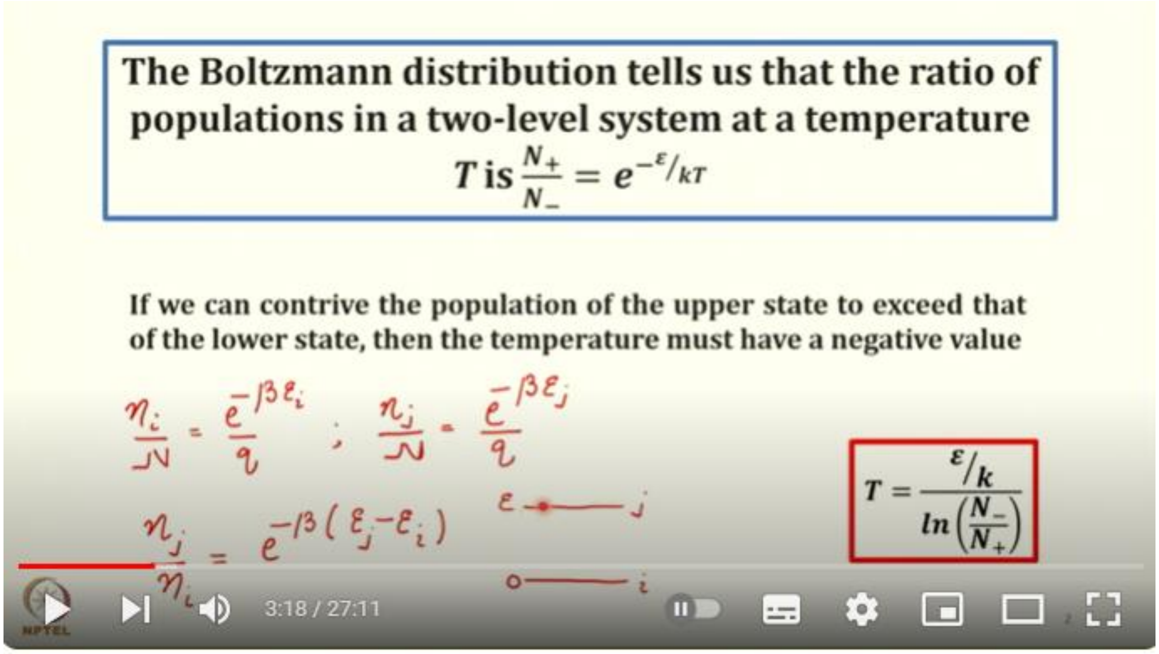

The Boltzmann distribution tells us that the ratio of populations in a two-level system at a temperature T is $\frac{N_+}{N_-} = e^{-\varepsilon/kT}$

If we can contrive the population of the upper state to exceed that of the lower state, then the temperature must have a negative value

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} \; ; \; \frac{n_j}{N} = \frac{e^{-\beta\varepsilon_j}}{q}$$

$$\frac{n_j}{n_i} = e^{-\beta(\varepsilon_j - \varepsilon_i)}$$

$$\boxed{T = \frac{\varepsilon/k}{\ln\left(\frac{N_-}{N_+}\right)}}$$

So, I will have exponential minus β E_j minus E_i. So, this way I can write the ratio of populations in a two-level system, I will now talk about in terms of temperature. So, the systems that we are talking about, let us say 1 and 2. If I call this ith state, I call it jth state. I can also look at it this way that this is 0 of energy E(0) and this is separated at energy E. And now based upon what I have derived over here, it is the ratio of the population of two states. And if I consider this two-level system in which you have ground state and you have first or upper excited state at an energy E, then how do I write the population? Consider again, let us write down these two states. This is 0, this is E and let us say the population or number of molecules in the upper state is n_+ and the lower state is n_-. Let us for the sake of convenience write like this. Then as we just discussed, n_+ divided by n_- is going to be exponential minus E upon k T.

We just derived the expression for the ratio of populations in a two-level system. Let us take a logarithm of this. If I take a logarithm of this, I have log n_+ n_- is equal to minus E upon kT. Let us consume negative sign. So, then I can write log n_- over n_+ is equal to E upon k T.

I have consumed minus sign and inversed this n_+ and n_-. Let us rearrange for temperature. Now temperature from this is E upon k divided by log n_- over n_+. So, we have got an expression now for temperature which is equal to E by k divided by log n_- divided by n_+. Now you carefully look at this expression that we derived.

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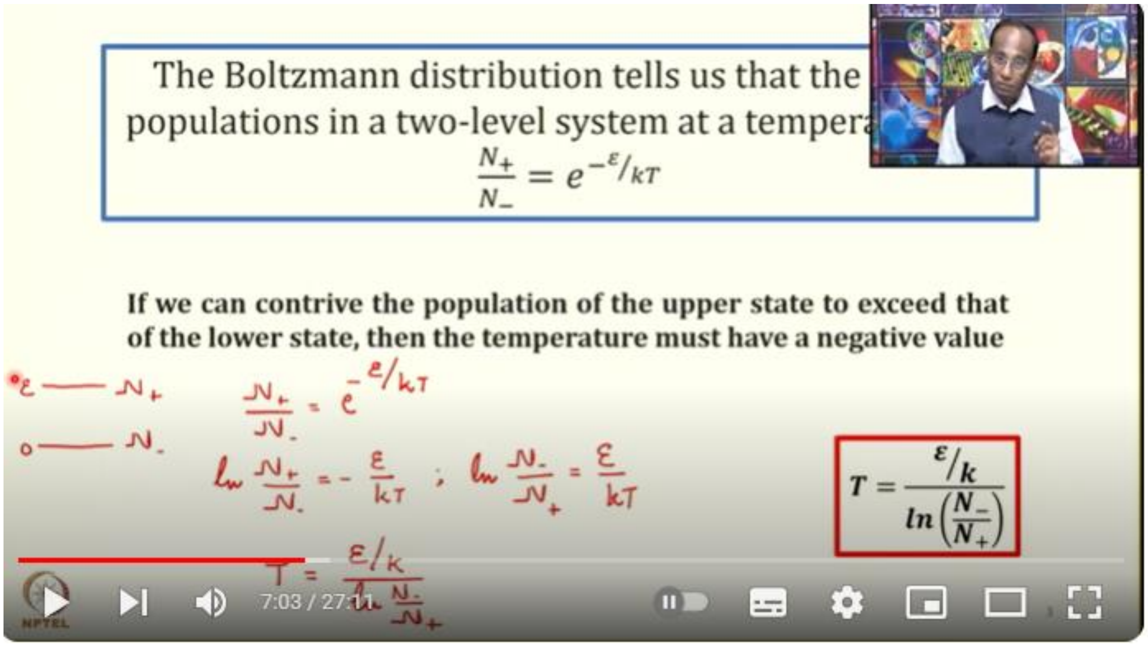

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ε —— N_+

0 —— N_-

$$\frac{N_+}{N_-} = e^{-\varepsilon/kT}$$

$$\ln\frac{N_+}{N_-} = -\frac{\varepsilon}{kT} \; ; \; \ln\frac{N_-}{N_+} = \frac{\varepsilon}{kT}$$

$$T = \frac{\varepsilon/k}{\ln\frac{N_-}{N_+}}$$

$$\boxed{T = \frac{\varepsilon/k}{\ln\left(\frac{N_-}{N_+}\right)}}$$

That is, if n_+ is higher than n-, if n_+ that means if we can contrive the population of the upper state to exceed that of the lower state, n_+ higher than n_- means somehow if we find out a way in which the population of the upper state exceeds that of the lower state, that means in that case this term is negative and the temperature can be negative. So according to this, if we can devise a method in which the population of the upper state can exceed that of the lower state, then the temperature must be negative. That means according to this, if we consider this two-level system, then in such case the negative temperature is possible. Now let us discuss what is the meaning of this negative temperature. That is temperature with a negative value.

Remember we are not talking about temperature in °Celsius. We are here talking about absolute temperature in Kelvin. What we are discussing here that if the upper state has more population than the lower state in a two-level system, then in that case the temperature has to be negative. Let us discuss further about this. So, what we have now, all the statistical thermodynamic expressions that we have derived apply to T less than 0 as well as T greater than 0.

What is the meaning of this comment? We have derived by now quite a few expressions, thermodynamic expressions in a statistical connection, partition function, we have derived expression for internal energy, we have derived expression for entropy and in each case, we were able to connect these thermodynamic quantities or partition function with temperature and nowhere we mentioned that the temperature has to be positive or temperature has to be negative. That means all the statistical thermodynamic expressions that we have derived so far apply to both T less than 0 and T greater than 0. But we will now soon discuss that the meaning of those quantities, how does it change when we apply to T greater than 0 or when we apply to T less than 0. Let's look at the next comment. The states with T less than 0 are not in thermal equilibrium.

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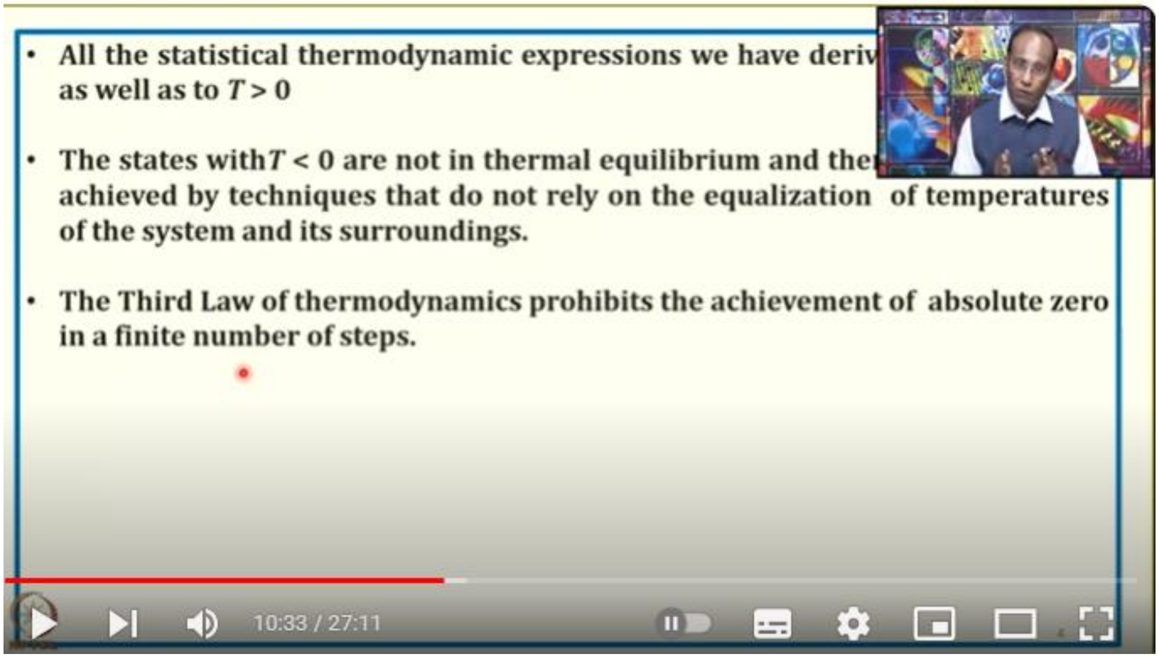

- All the statistical thermodynamic expressions we have deriv as well as to $T > 0$
- The states with $T < 0$ are not in thermal equilibrium and the achieved by techniques that do not rely on the equalization of temperatures of the system and its surroundings.
- The Third Law of thermodynamics prohibits the achievement of absolute zero in a finite number of steps.

This is important to recognize. The states with T less than 0 are not in thermal equilibrium and therefore have to be achieved by techniques that do not rely on equalization of temperatures of the system and its surroundings. So, these non-thermal equilibrium states, this is beyond the scope of current discussion you will study at higher level, but for the time being you assume or you believe that the states with less than 0 absolute temperature are not in thermal equilibrium. And therefore, different type of techniques will have to be used to achieve negative temperature. We will discuss very briefly about that.

The third law of thermodynamics prohibits achievement of absolute 0 in a finite number of steps. This is a good time when we should revisit the third law of thermodynamics. The third law of thermodynamics says entropy of each substance is positive which may become 0 and it does become 0 at absolute 0 for perfectly crystalline substances. An alternate form of the third law of thermodynamics that we discussed in chemical thermodynamics was that it is impossible to achieve absolute 0 in a finite number of steps. And what is that? Let's take a quick look on that.

This one is a plot of entropy versus temperature. At temperatures above 0, in general the entropy increases with rise in temperature. So therefore, if we consider the conditions where the sample is not subjected to any magnetization and the sample has lots of unpaired electron, un-magnetized, whatever is its extent of unpaired electrons, let's call it more disordered state. Now obviously when you subject this substance to magnetization, that is you switch the magnetic field on, there will be more orientation of electrons in the direction of applied field. So therefore, there will be more order, it will be less disorder, therefore entropy will be less and entropy temperature curve will behave like this.

For the magnetized sample, the entropy temperature curve will be lower than that for the un-magnetized sample. Let us consider the process which is used to achieve very low temperature. Once again recalling the concepts that we developed in chemical thermodynamics, that you can easily achieve 4 Kelvin because that is the boiling point of helium. And then when you pump helium through large diameter pipes and when the helium is pumped, it will draw energy from the pipes and produce cooling. So, as I said, if you pump helium through large diameter pipes, you can bring down the temperature to 1 Kelvin.

Now below 1 Kelvin, what we need is adiabatic demagnetization and let us first talk in terms of electronic spins. Consider first that we have a sample for which the entropy temperature curve is blue 1 and we start with point A. At point A, carry out isothermal magnetization process. Remember what I am saying is isothermal magnetization process. Isothermal means temperature should remain constant.

How will this temperature remain constant? That helium will provide a link between the source and the sink. Extra energy which is liberated can be discarded or extra heat which is liberated can be discarded to the surroundings, to the sink. So, when we carry out isothermal magnetization, isothermal means it has to follow this horizontal line, constant temperature. And when you carry out magnetization, the corresponding point on the magnetized entropy temperature curve of the sample will be B. A to B, it is isothermal magnetization.

Next step is important. Next step, ensure reversibility. And now you remove the magnetic field very very very slowly in a reversible manner under adiabatic conditions. Note what I am saying. Remove the magnetic field, switch off the magnetic field very slowly in a reversible manner under adiabatic condition. That is why this term adiabatic demagnetization is given.

How now it will affect the thermodynamic quantities? Remember Clausius inequality. What was that? dS is greater than or equal to dQ by T. And if I am ensuring reversibility, that means dS is equal to dQ_{rev} by T. That is how we interpret this Clausius inequality. That is the equality holds for reversibility.

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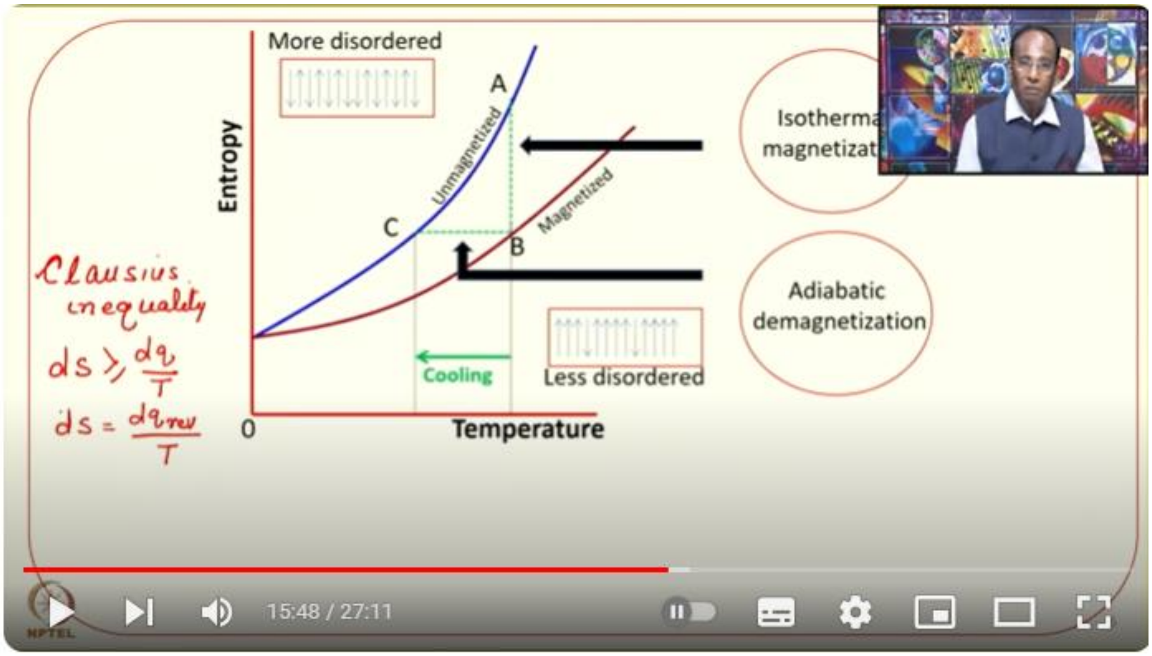

Isotherma
magnetizat

Adiabatic demagnetization

Clausius inequality

$$ds \geq \frac{dq}{T}$$

$$ds = \frac{dq_{rev}}{T}$$

And if the process is reversible, if it is adiabatic, that means no heat is allowed to be exchanged between system and surrounding. dQ is equal to 0. If dQ is equal to 0, dS are equal to 0, that means the process becomes isentropic. The entropy does not change.

No. Therefore, if the entropy does not change and you remove the magnetic field, the entropy does not change, that means it has to remain horizontal here, horizontal behavior. The corresponding point on the unmagnetized entropy temperature curve is C. Now, again carefully examine what has happened from B to C is that the temperature has decreased. There is cooling, cooling which has produced. So, what is done here is we need to have a paramagnetic material as we discussed here.

We need a lot of electrons which are creating paramagnetic behavior. And the sample of paramagnetic material can be D or F metal complex. Example is gadolinium sulfate octa hydrate. It will have lots of unpaired electrons. And as I just mentioned, first we cooled to about 1 Kelvin.

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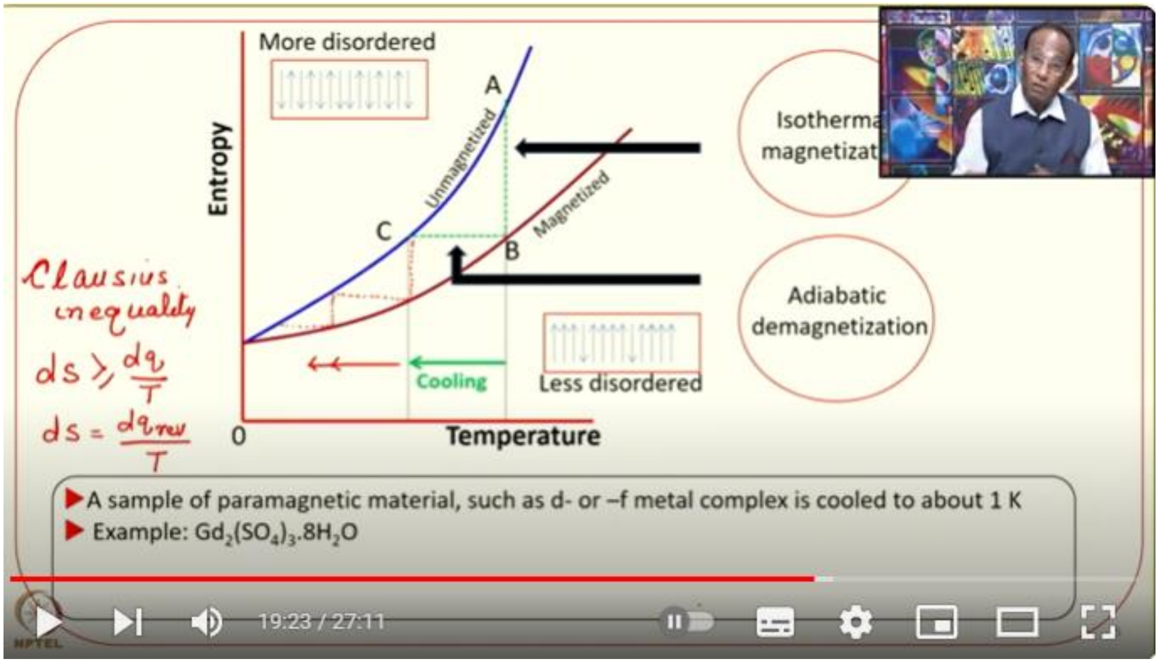

Clausius inequalty

$ds \geq \frac{dq}{T}$

$ds = \frac{dq_{rev}}{T}$

- A sample of paramagnetic material, such as d- or –f metal complex is cooled to about 1 K
- Example: $Gd_2(SO_4)_3.8H_2O$

That process I also discussed just now. And below 1 Kelvin, what we need is adiabatic demagnetization process. We have just discussed one step. First is isothermal magnetization, second is adiabatic demagnetization. And in this sequence of two steps, what we observe is that cooling has been produced.

So obviously, now if we repeat these steps, what will happen? If we repeat these steps, let's say carry out again magnetization, then adiabatic demagnetization, another cooling will be produced, then again magnetization, demagnetization, again cooling will be produced. That means we will keep on moving towards lower and lower temperature. What I have discussed over here is basically the spin of the electrons. This example also highlights the applications, technological applications of the third law of thermodynamics. See how nicely this third law of thermodynamics is explaining the process of achieving very very low temperature.

Why am I discussing this? Because we just discussed one highlight that according to third law of thermodynamics, it is not possible to achieve absolute zero in finite number of steps. And if you look at here the number of steps, that I will describe in the next slide that under what conditions in finite number of steps you can achieve zero, whether those conditions are possible or not. But before that, as I was talking to you that here we have used the electrons, but the temperature, lower temperature, so what is the world record minimum temperature achieved so far? The reported lowest temperature achieved so far is of the order of Pico Kelvin, 10 raised to the power minus 12 Kelvin. The process that we are discussing is 4 Kelvin liquid helium, 1 Kelvin pumping helium through large diameter pipes, below 1 Kelvin we are using the electronic magnetic moments, but the temperature of the order of pico Kelvin that I am talking about uses the nuclear magnetic moments. That means the term there will be adiabatic nuclear demagnetization.

Whether it is electronic demagnetization or it is nuclear demagnetization, the process is same, we need several cycles to lower the temperature. Now let's talk about why it is not possible to achieve absolute zero in a finite number of steps. What is the other form of third law of thermodynamics? Is that entropy of every substance is positive, I am repeating this, which may become zero and thus become zero at absolute zero for perfectly crystalline substances. That means the entropy temperature curve have to merge at absolute zero. Now this zero is for the temperature scale, not for the entropy scale.

For entropy scale I will put zero over here, they are merging here, some value which we are referring to as zero. And if you look at now the number of steps, first step, second step, third step, you keep on doing. In order to achieve absolute zero, you need infinite number of steps. That is why the alternate form of third law of thermodynamics that it is not possible to achieve absolute zero in finite number of steps. But if you look at the left-hand side figure, if the entropy temperature curve were to vary like this, that they do not merge at absolute zero, then it is possible to achieve absolute zero in finite number of steps. But then you are violating the third law of thermodynamics which says that they must merge for perfectly crystalline substances. So therefore, the right-hand side figure suggests that it is not possible to achieve absolute zero in a finite number of steps. No one has ever succeeded in cooling any system to absolute zero and the reason for that we have just discussed. And the third law, it is impossible to reach T equal to zero in a finite number of steps.

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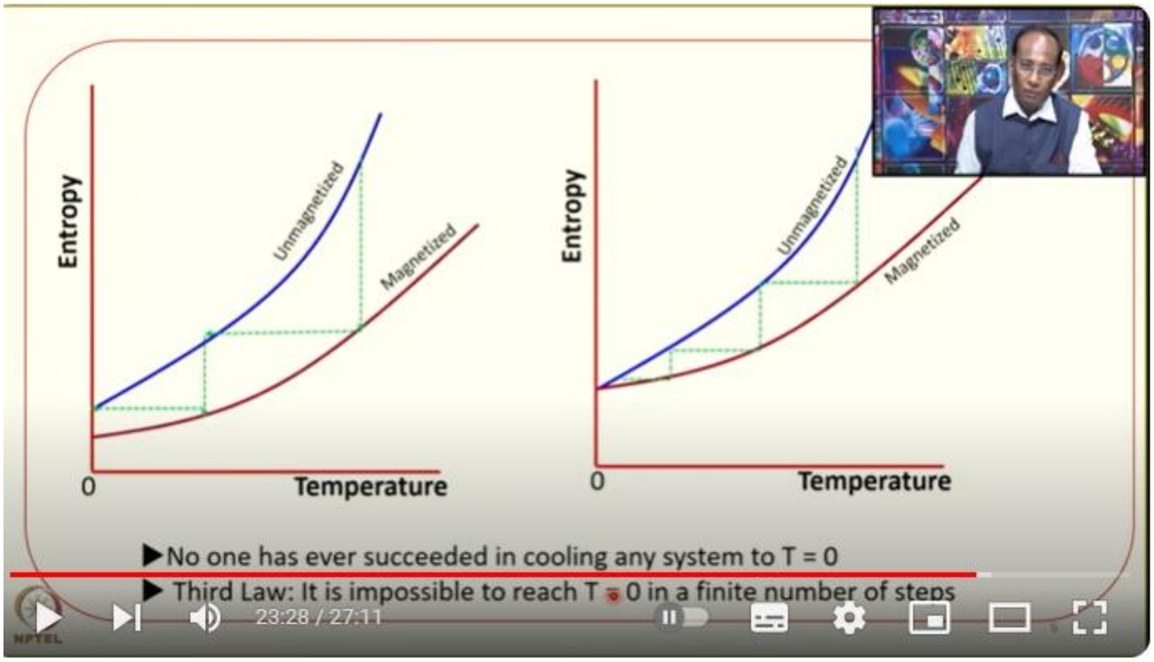

- ▶ No one has ever succeeded in cooling any system to T = 0
- ▶ Third Law: It is impossible to reach T = 0 in a finite number of steps

And that is what we were discussing over here. We were at this highlight that the third law of thermodynamics prohibits the achievement of absolute zero in a finite number of steps. Let's look at the next important highlight which says that however it is possible to circumvent this restriction in systems that have a finite number of levels or in systems that are effectively finite because they have such weak coupling to their surroundings. As I will soon show in the next lecture that it is possible to circumvent this restriction, but the systems chosen will be such that they have finite number of levels. For example, you know easiest one for us is to choose a two-level system and then demonstrate. The practical realization of such a system is a group of spin half nuclei that have very long relaxation times.

So pulse techniques in NMR can achieve non-equilibrium populations as can pumping procedures in laser technologies. So, these two methods that I have discussed over here we are not going to cover in this course. You will study in the advanced level when you will learn NMR and pumping procedures in laser technologies. There you will talk more about that. So again, emphasizing on that the expressions that we derived for example for Q in terms of temperature or U in terms of β, β is essentially 1 over kT or S we have talked in terms of temperature and partition function which is essentially again described in terms of temperature.

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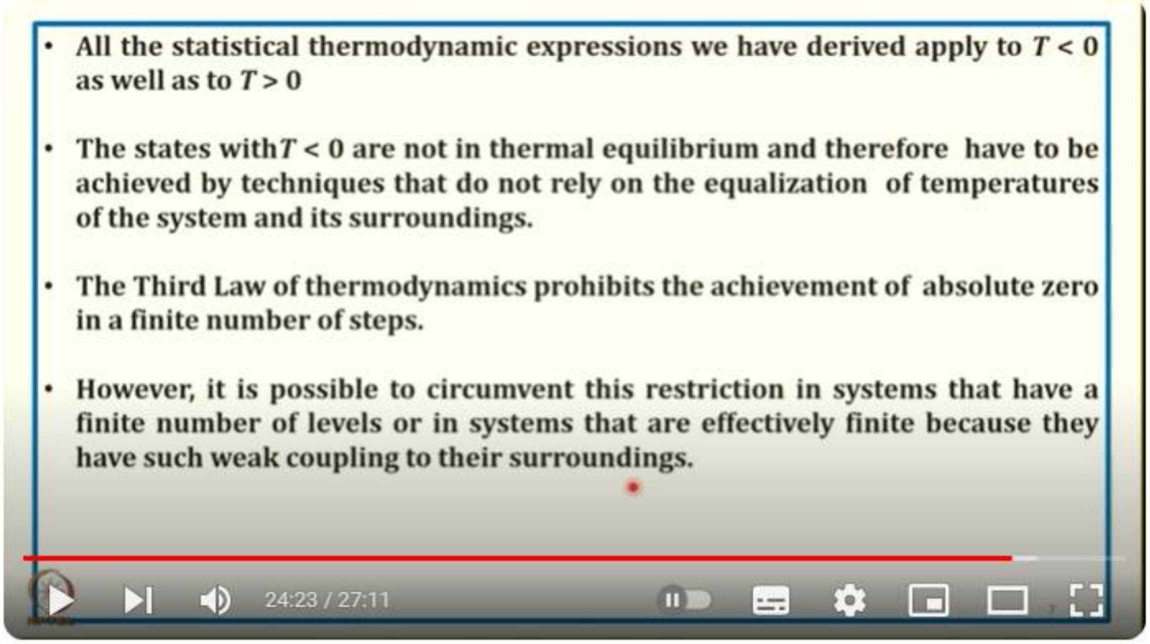

- **All the statistical thermodynamic expressions we have derived apply to $T < 0$ as well as to $T > 0$**
- **The states with$T < 0$ are not in thermal equilibrium and therefore have to be achieved by techniques that do not rely on the equalization of temperatures of the system and its surroundings.**
- **The Third Law of thermodynamics prohibits the achievement of absolute zero in a finite number of steps.**
- **However, it is possible to circumvent this restriction in systems that have a finite number of levels or in systems that are effectively finite because they have such weak coupling to their surroundings.**

In the derivation of these equations we never said that these equations are not valid for T is equal to 0 or T less than 0. The expressions for Q, U and S are applicable both for T less than 0 and T greater than 0. But then what does it mean? What is the meaning of negative temperature? That we will discuss in the next lecture and how this negative temperature can affect the variation of partition function with temperature or variation of internal energy and entropy with temperature. We will discuss these in the next lecture. Thank you.