Interfacial Engineering

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Lecture-17

Thermodynamic principles of self-assembly

CMC; Gibbs free energy of micellization; Enthalpy of micellization; Gibbs-Helmholtz relationship

Welcome back. In today's video lecture, we will look at the thermodynamic principles of self-assembly. In short, we can also alternatively call it the thermodynamics of micellization. Okay, because we know that at some concentration, surfactant molecules self-assemble to form micelles. The process of forming micelles is nothing but micellization. So, we can look at some thermodynamic concepts behind this process, you know, micellization.

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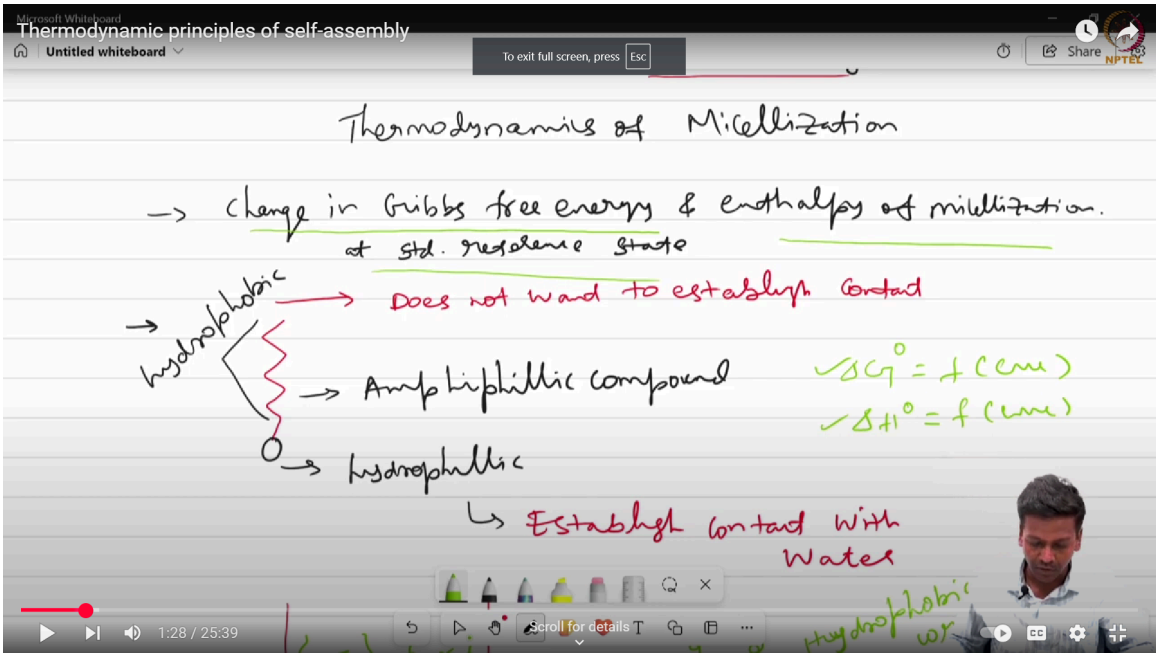

So basically what we will be interested in is we will try to find out what is the change in Gibbs free energy and enthalpy of micellization at standard reference state. We will try to find out what is the change in Gibbs free energy as a function of CMC and what is the enthalpy change in enthalpy at as a function of CMC both are measured at some standard reference state. Let's begin, we will look at some of the important concepts before we move on to the thermodynamic aspects so we will try to understand what is critical micellar concentration. So, first of all, we know that there are two counteracting you know components you would say that the surfactant is nothing but an amphiphilic compound that we know consists of two parts right, one is nothing but hydrophilic and is water-loving and the other one is hydrophobic which is oil loving right so these two counterparts so when you disperse this or dissolve this surfactant into, let's say solvents like water or any medium so because this is hydrophilic is water loving it would want to maximize its exposure with water molecule we're talking about aqueous solution here now, on the other hand, the hydrophobic part would want to minimize its contact with the water molecule right so

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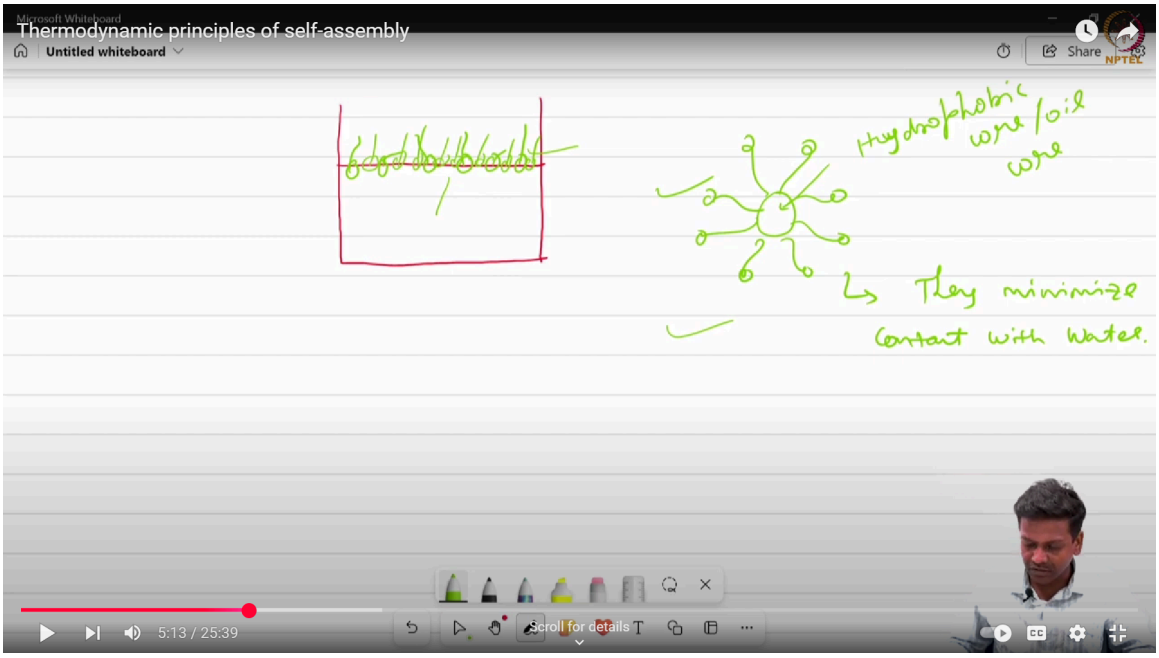

This is the reason why they have a natural tendency to you know self assemble, say whenever we add surfactant when we prepare and acquire a solution of surfactant. Surfactants have a natural tendency to go to the interface and you know, orient themselves such that the hydrophobic part is kept away from the contact with water, right? In this way, they minimize the contact of the hydrophobic part with water. So this is the natural tendency, right, for surfactant. Now the question comes, what if we keep adding the surfactant into the aqueous solution? So beyond some concentration, when they, you know, arranged in a condensed manner so because there is not going to be any space available beyond some concentration right so whatever we add further what will happen is they will go on making they will go to the bulk the surfactant will go to the bulk.

As soon as they go to the bulk, they, you know, combine, right? Combine to form micelles, self-assemble to form micelles in this way. So, this is nothing but a micelle. So when they assemble, self-assemble in this fashion or self-organize in this fashion, they would try to minimize their exposure or contact with the water molecule, right? So in this way, you know they can avoid contact with the water molecule that's why as soon as we add surfactant into the aqueous solution they will go to the interface and try to minimize

the contact when we add further and further because now there is no further space available or the surface concentration has reached the saturation level they will go to the bulk but since they are in the bulk so they will be forced to self assemble so that they can minimize the exposure with water molecules. This is the reason why they self-assemble to form micelles now. Now there is going to be a transition and this is going to be an equilibrium process. When we keep adding the surfactant into the aqueous solution because it tries to go to the interface and remain at the interface beyond some concentration, the surface concentration will remain the same because whatever we add further goes into the bulk, right? Whatever we add further goes into the bulk.

And whatever has gone into bulk, try to self-assemble to form micelles, right? So, this is the idea. At equilibrium, the rate at which the monomer goes to bulk-forming micelle and the monomer goes from bulk to interphase will be the same, which means that the surface concentration remains intact. Okay, even though we add, you know, I mean more and more surfactant, but what will happen is there will be micelles will be growing, right? So, the number of micelles will go up.

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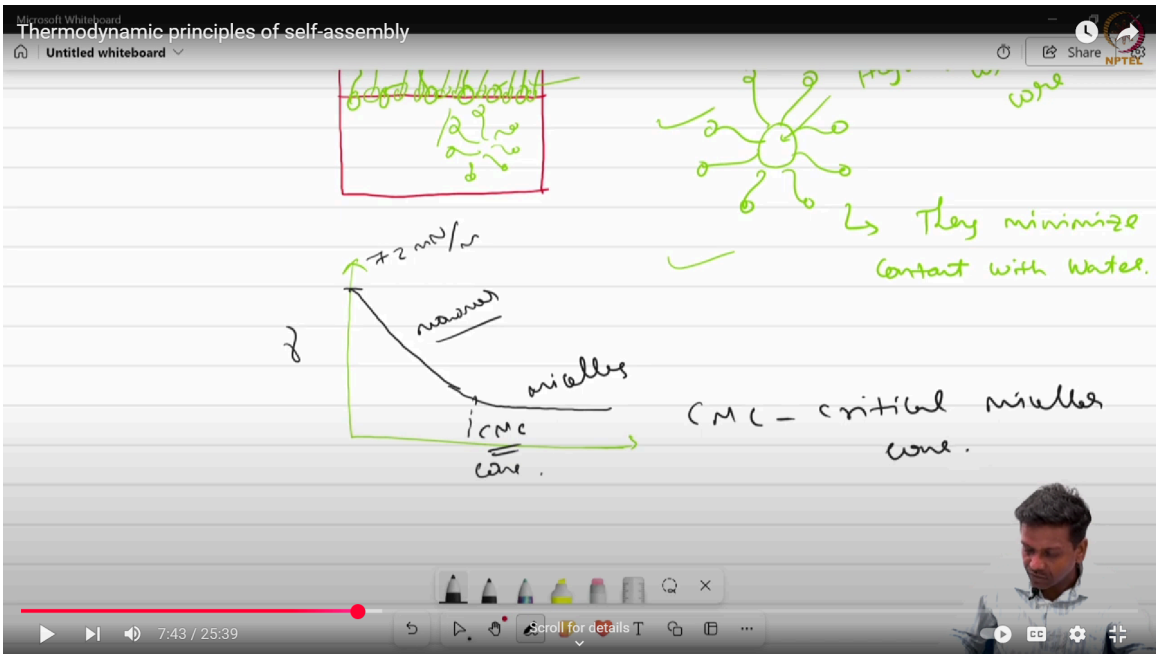

Okay, so if I have to understand this transition, basically what I can do is I can use this, you know, I can measure the interfacial property like, you know, γ, which is surface tension as a function of concentration, right? So what will happen, let's say if I take about example of let's say air-water interface, so that is nothing but, you know, usually it will be around 72 mN/m. So because you add more concentration, the surface tension goes down and then it will reach a stage where the surface tension that you measure remains the same because the surface concentration going to remain the same. Whatever you add further will not contribute, will not get absorbed at the interface, they will go into the bulk, so this transition, right, the point at which this transition occurs, that is monomer to micelles, so this point is nothing but CMC, which is CMC is nothing but critical micellar concentration. There are other techniques that you can use. Say for example, you can also measure the properties in bulk.

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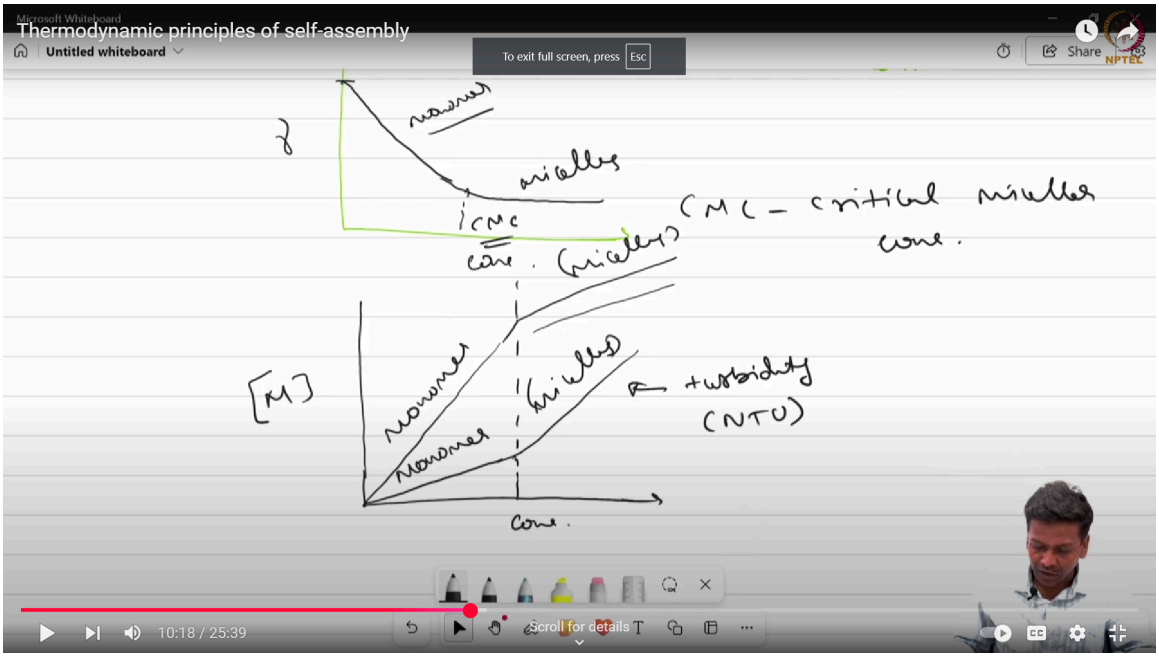

So let's say if you want to measure some property in the bulk, let's say some property we measure in the bulk and as a function of concentration. For example, I am talking about turbidity.

Turbidity is so in this way you can see that there is a change in the slope because we use the turbidity meter which measures the NTU units and this indicates the measure of cloudiness in the solution and turbidness in the solution because when they are in the monomer state right in the bulk. There will not be a solution and it will not become turbid but as soon as they form micelles which are nothing but an aggregate solution start to turn you know turbid right from the clear state to turbid state you know one can observe this transition from clear state to turbid state using the turbidity meter so at this point what we measure is nothing but CMC which is nothing but critical micellar concentration so no matter which technique you use the CMC is going to be the same. For example, if I use the conductivity meter right in this case also you would see that the CMC is measured at the same point, and because when you use the conductivity meter using the let's say connectivity probe what will happen is as soon as the surfactant is in monomer state because it doesn't hinder the ionic movement you would see that the slope here is the rate at which the conductivity increases is higher than the rate at which the connectivity increases in this case of you know the domain where micelles are formed right. So you can say that the point at which this transition occurred from the monomer to micelle is nothing but critical micellar concentration and these two properties are measured in the bulk.

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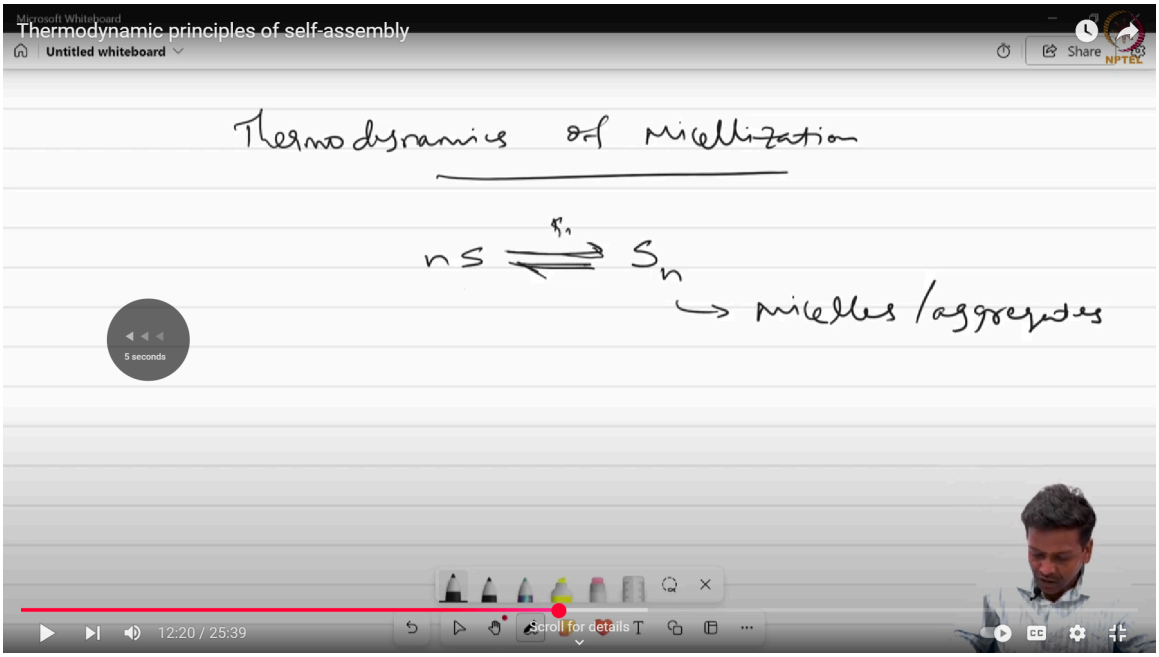

Now, let's examine the known thermodynamics of micellization. During this process, surfactant monomers aggregate to form micelles, which are essentially aggregate structures. We can apply a reaction approach to represent this scheme. For instance, in polymerization reactions, monomers are converted into polymers. If you have *n* monomers, you end up with a polymer consisting of *n* segments. This is the straightforward reaction approach used in polymerization.

Similarly, we can consider surfactant molecules as monomers. These individual molecules can be represented using notation analogous to polymers, but in this context, they form micelles or aggregates containing multiple monomer molecules or surfactant molecules. We use equilibrium notation because micellization is an equilibrium process. At equilibrium, any additional surfactant added will be distributed between the bulk phase and the micelles. The rate at which monomers enter the bulk phase is equal to the rate at which monomers from the bulk phase join the micelles, reflecting the equilibrium state.

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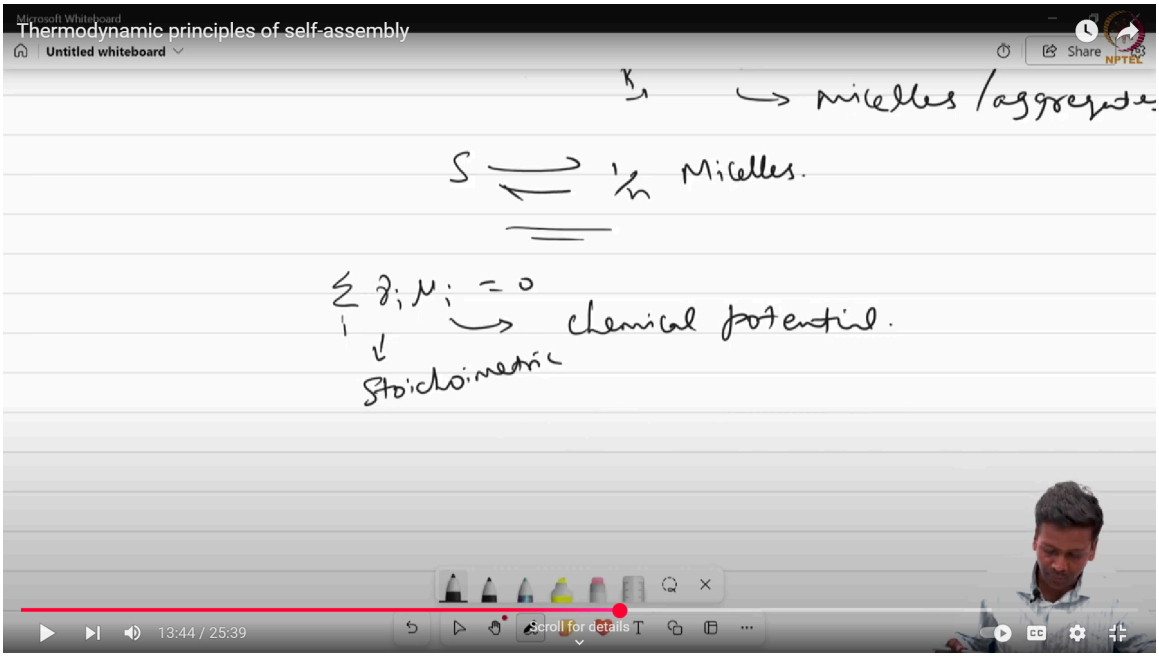

If we apply this reaction approach, we can represent the process as monomers forming micelles. Let's start with the criterion for equilibrium in any equilibrium reaction. This involves understanding that at equilibrium, the rates of forward and reverse reactions are equal. In the context of micellization, this means that the rate at which monomers join the micelles is equal to the rate at which monomers leave the micelles.

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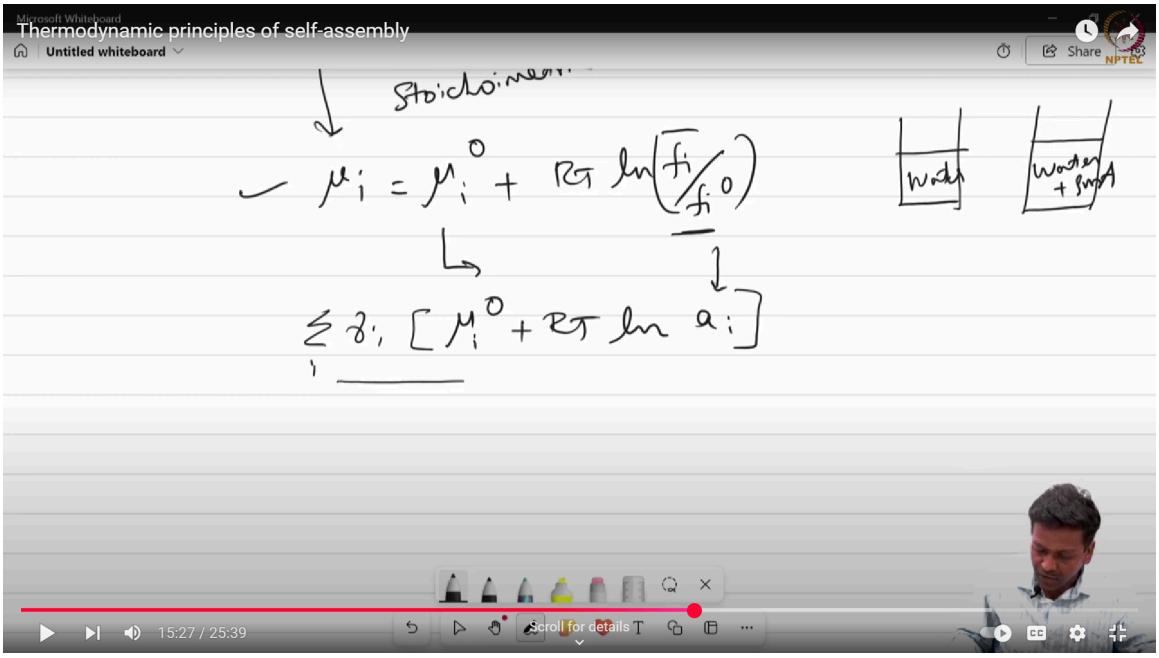

We know that the criterion for equilibrium is expressed as:

$$\sum \gamma_i \mu_i = 0$$

Here, γ_i is the stoichiometric coefficient, and μ_i Is the chemical potential. Applying this to our case, we can write:

$$-\mu_1 + \mu_2 = \Delta\mu = 0$$

This follows the convention of assigning negative coefficients for reactants and positive coefficients for products. This equation represents the equilibrium criterion.

Now, starting from $\sum \gamma_i \mu_i = 0$, we know that for a mixture, the chemical potential μ_i This can be expressed as:

$$\mu_i = \mu_i^0 + RT ln \frac{f_i}{f_i^0}$$

Here:

- μ_i^0 Represents the chemical potential measured at the same temperature for a standard reference state (e.g., pure water).

- The binary mixture in this case consists of surfactant and water.

Substituting this expression into the equilibrium equation $\sum \gamma_i \mu_i = 0$ Gives terms involving: $RTln\frac{f_i}{f_i^0}$

We know that $\frac{f_i}{f_i^0}$ is equivalent to the activity a_i, where activity is defined as:

$a_i = \frac{fugacity\ of\ mixture}{fugacity\ at\ standard\ reference\ state}$

Thus, we can replace $\frac{f_i}{f_i^0}$ with a_i

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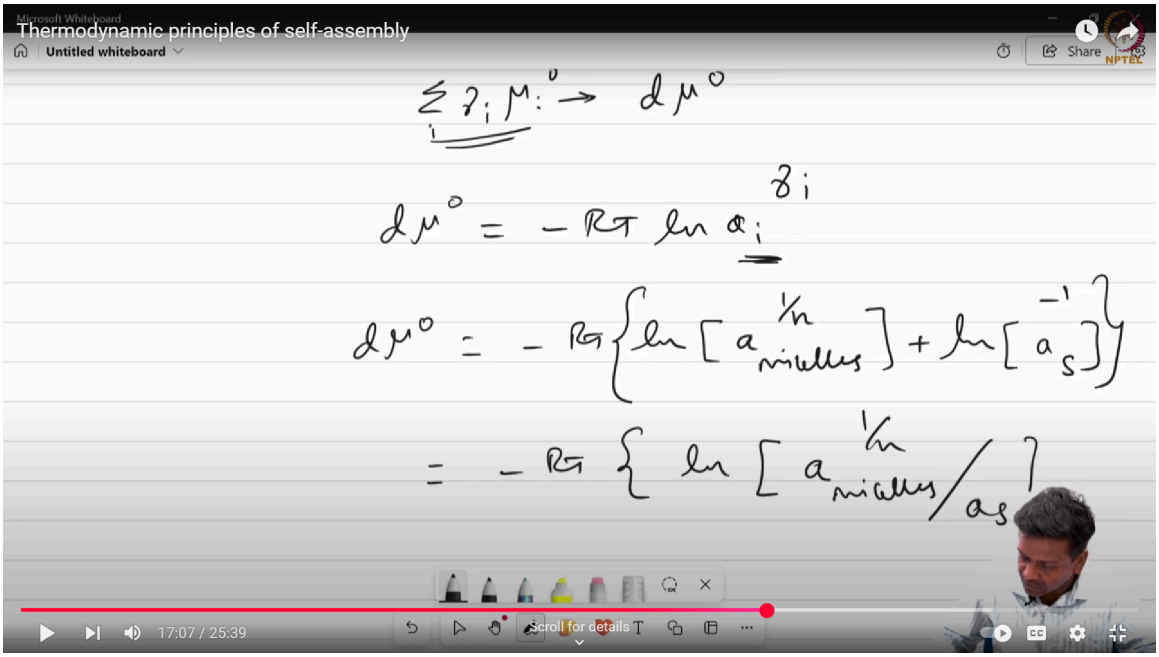

So, if we decompose this into a summation over i, we have: $\sum_i \mu_i^0$

This simplifies to $\Delta\mu^0$ Because, for stoichiometry, we use the convention of negative coefficients for reactants and positive coefficients for products. Therefore, this becomes: $\Delta\mu^0$

We can express this as: $\Delta\mu^0 = -RTln\prod_i a_i^{\gamma_i}$

Now, we can use this expression as is. From here, we can proceed with two more steps to explicitly express the activity for micelles and surfactants.

If we explicitly express this for micelles, the stoichiometric coefficient γ_i in this case, will be $\frac{1}{n}$ For the micelles. So, we can write: $\gamma_i = \frac{1}{n}$

For the surfactants, it will be -1, reflecting the convention for reactants. Therefore, we can express the activity term as: $ln\left(\frac{a_{micelles}^{1/n}}{a_{surfactant}}\right)$

This simplifies to:

$$\frac{1}{n}lna_{micelles} - lna_{surfactant}$$

Thus, we can write this as:

$$\frac{1}{n}lna_{micelles} - lna_{surfactant} = \frac{1}{n}lna_{micelles} - lna_s$$

Where a_s Represents the activity of the surfactant monomers.

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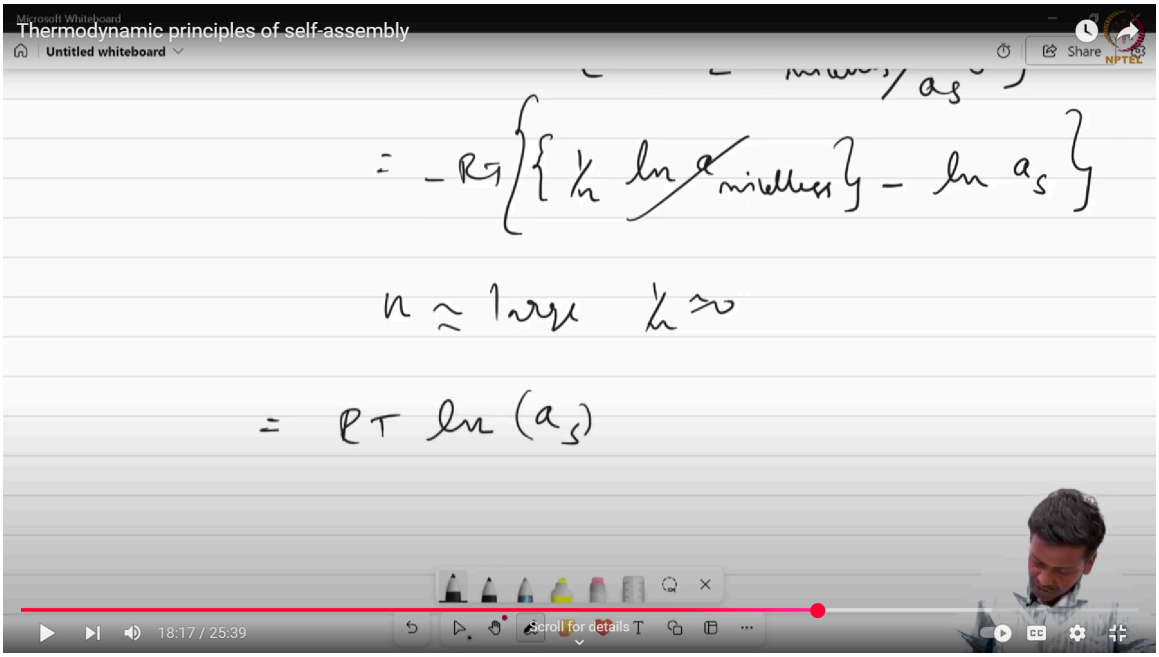

Okay, so we can write this as: $-\ RTln\left(\frac{a_{micelles}^{1/n}}{a_s}\right)$

We can decompose this further into: $-\ RT\left(\frac{1}{n}lna_{micelles}\ -\ lna_s\right)$

This simplifies to:

$$-\ RT\left(\frac{1}{n}lna_{micelles}\right)+\ RTlna_s$$

Or, more explicitly

$$-\frac{RT}{n}lna_{micelles}+\ RTlna_s$$

Now, if we consider that n If the number of monomers, which is usually very large, then $\frac{1}{n}$ Becomes negligible. Therefore, we can ignore the term involving. $\frac{1}{n}$.

What remains is: $RTlna_s$

This is what we are left with.

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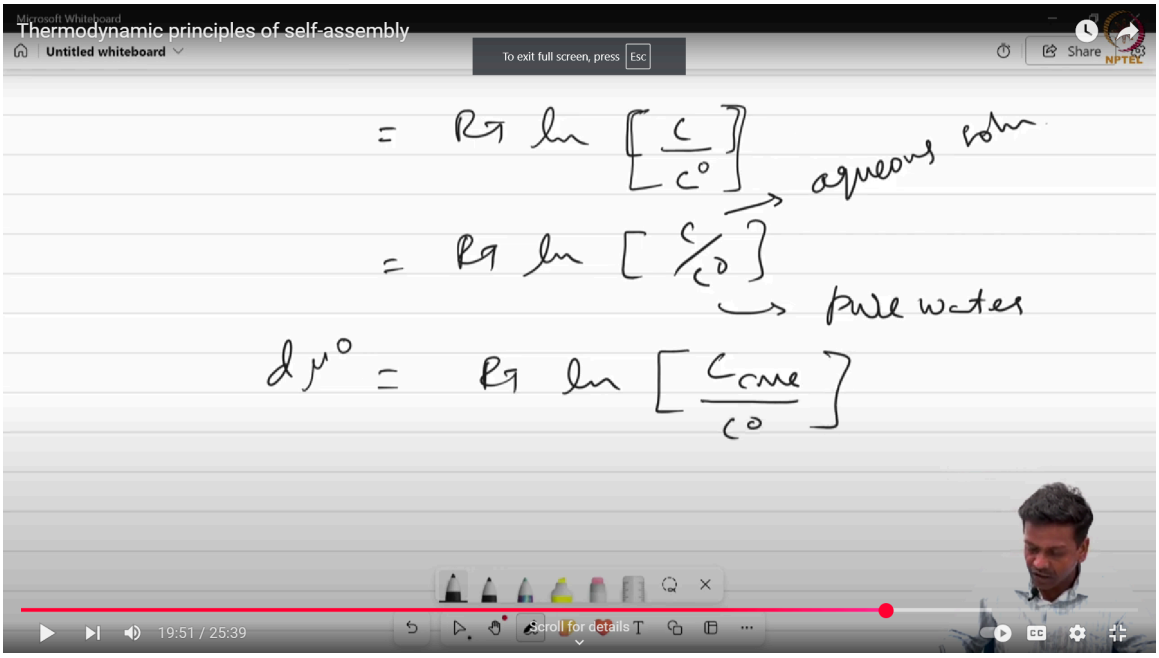

Now, we know that the activity can be expressed in terms of concentration. Remember, since we have a lone operator here, we want to normalize this with respect to some reference state. Usually, in textbooks, many don't explicitly mention a reference state, but if it's not mentioned, you should understand that it's normalized to one.

However, in this case, we can use a standard reference state to normalize this quantity, making it dimensionless. So, we can express the activity as:$a = \frac{C}{C_0}$

Where C_0 Is the concentration at the reference state, typically for pure water? This means that C Is the concentration in the aqueous solution, which is a binary mixture containing surfactant plus water.

Now, we have:

$$\Delta\mu^0 = RTln\frac{C}{C_0}$$

At equilibrium, we're talking about the critical micellar concentration (CMC). In this case, the concentration we measure is simply the concentration at the CMC, denoted as C_{CMC}. Therefore, we can express this as: $\Delta\mu^0 = RTln\frac{C_{CMC}}{C_0}$"

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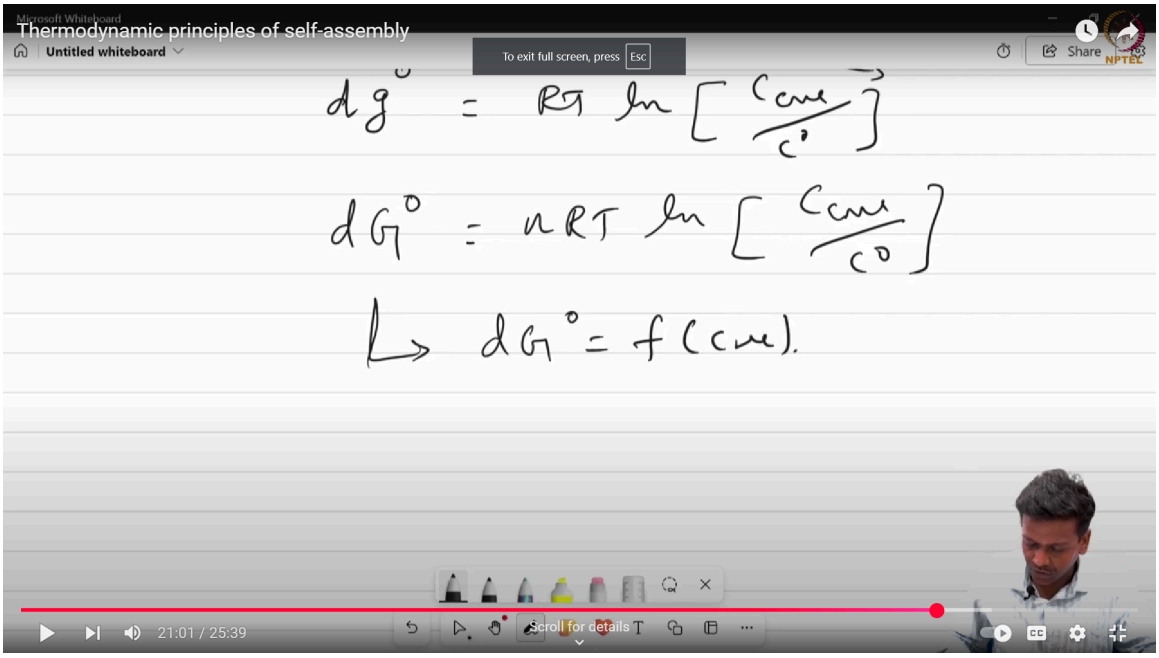

So we can return this concentration as it is. This is nothing but the concentration at the standard reference state, in this case, pure water. The term $\Delta\mu^0$ can also be represented as G^0, which is the molar Gibbs free energy. You can express this as:

$$\Delta\mu^0 = G^0 = RTln\frac{C_{CMC}}{C_0}$$

Sometimes, you can also use the notation where instead of molar energy, you use the Gibbs energy directly.

In that form, you would need to multiply by n, resulting in: $nRTln\frac{C_{CMC}}{C_0}$

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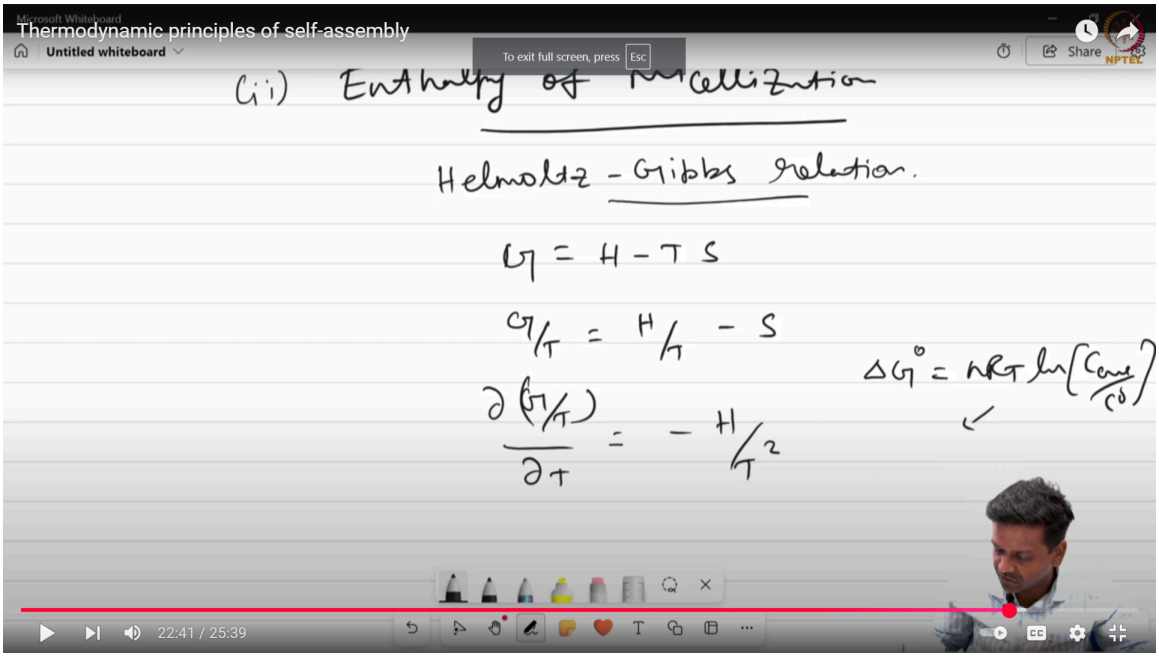

Now, we will look at the enthalpy of micellization. We examine the enthalpy of micellization. So, we are focusing on the enthalpy of micellization. To do this, we will borrow the concept from the Helmholtz-Gibbs relation. This relation states that the Gibbs free energy. G This can be expressed as:

$$G = H - TS$$

If we divide both sides by temperature T, we get: $\frac{G}{T} = \frac{H}{T} - S$

Deriving this concerning temperature gives us: $\frac{d}{dT}\left(\frac{G}{T}\right) = -\frac{H}{T^2}$

Recall that we have a relationship for ΔG^0, which is: $\Delta G^0 = nRTln\frac{C_{CMC}}{C_0}$

This relationship will help us further analyze the enthalpy of micellization.

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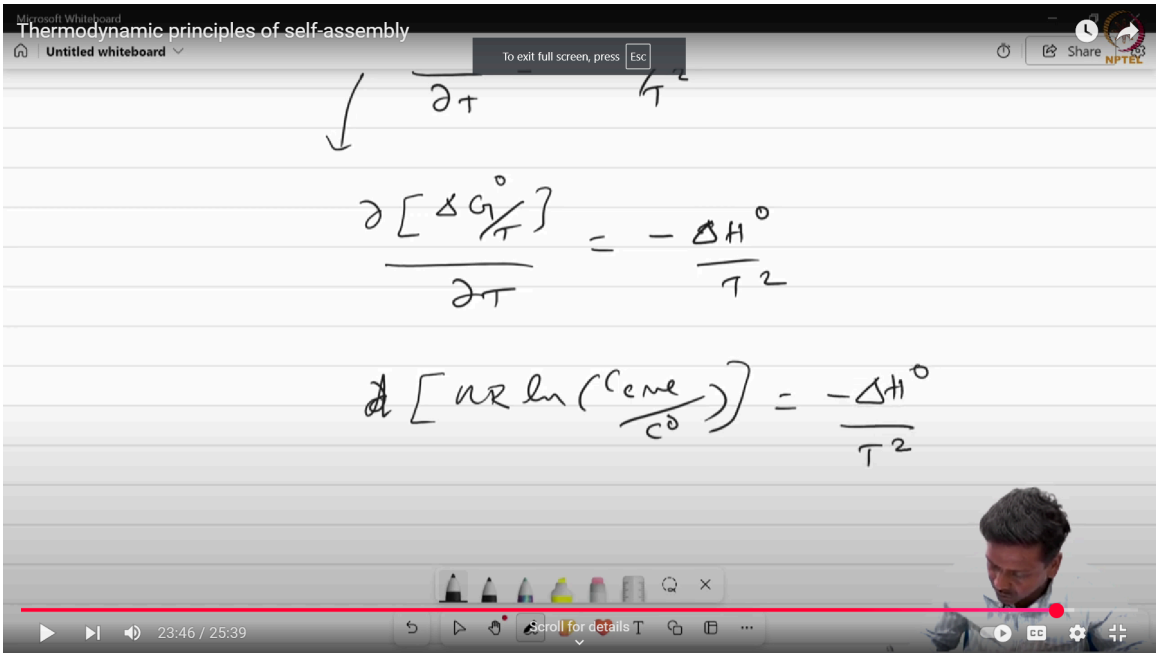

So, we want to use this expression. To do this, we need to modify both sides of the equation by using the derivative operator and incorporating the standard reference state notation.

We can modify the equation as follows: $\frac{d}{dT}\left(\frac{\Delta G^0}{T}\right) = -\frac{\Delta H^0}{T^2}$

This expression is in terms of the change in Gibbs free energy at the standard reference state. If we use the relationship for ΔG^0, we can express it as: $\Delta G^0 = nRTln\frac{C_{CMC}}{C_0}$

Substituting this into the derivative gives us: $\frac{d}{dT}\left(\frac{nRTln\frac{C_{CMC}}{C_0}}{T}\right) = -\frac{\Delta H^0}{T^2}$

Simplifying this, we can say: $nRln\frac{C_{CMC}}{C_0} \cdot \frac{dT}{T^2} = -\frac{\Delta H^0}{T^2} \cdot dT$

This can be further simplified to: $nRln\frac{C_{CMC}}{C_0} = -\frac{\Delta H^0}{T} \cdot dT$

However, the correct interpretation of your statement seems to be: $nRln\frac{C_{CMC}}{C_0} = -\frac{\Delta H^0}{T^2} \cdot dT$

This equation relates the change in Gibbs free energy to the enthalpy of micellization.

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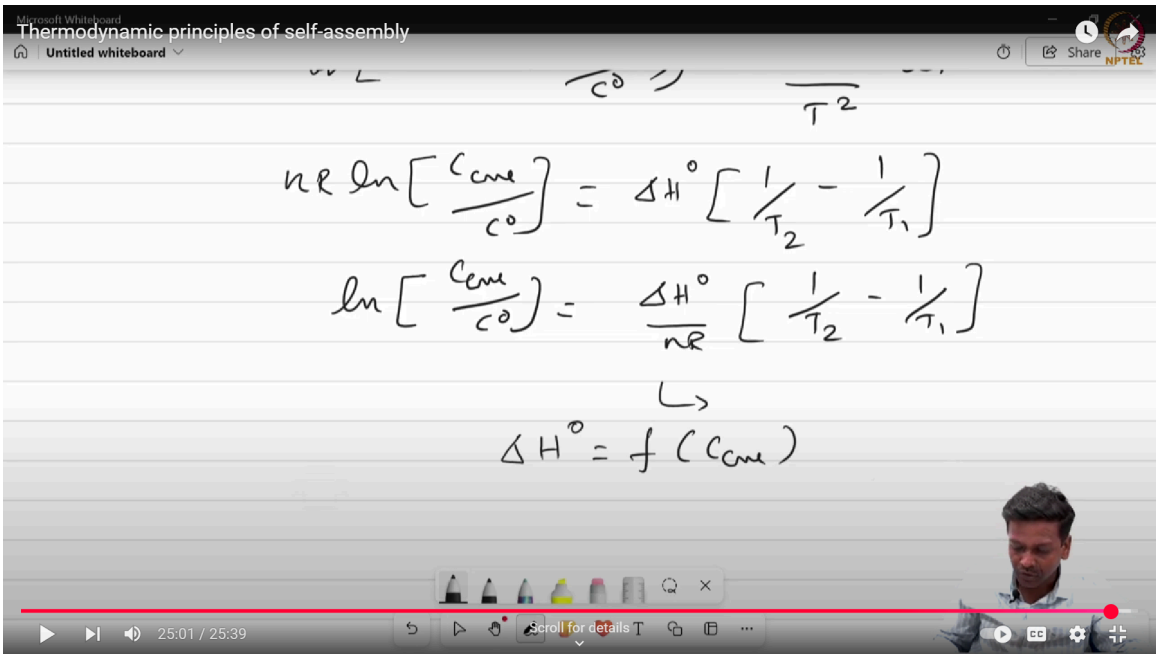

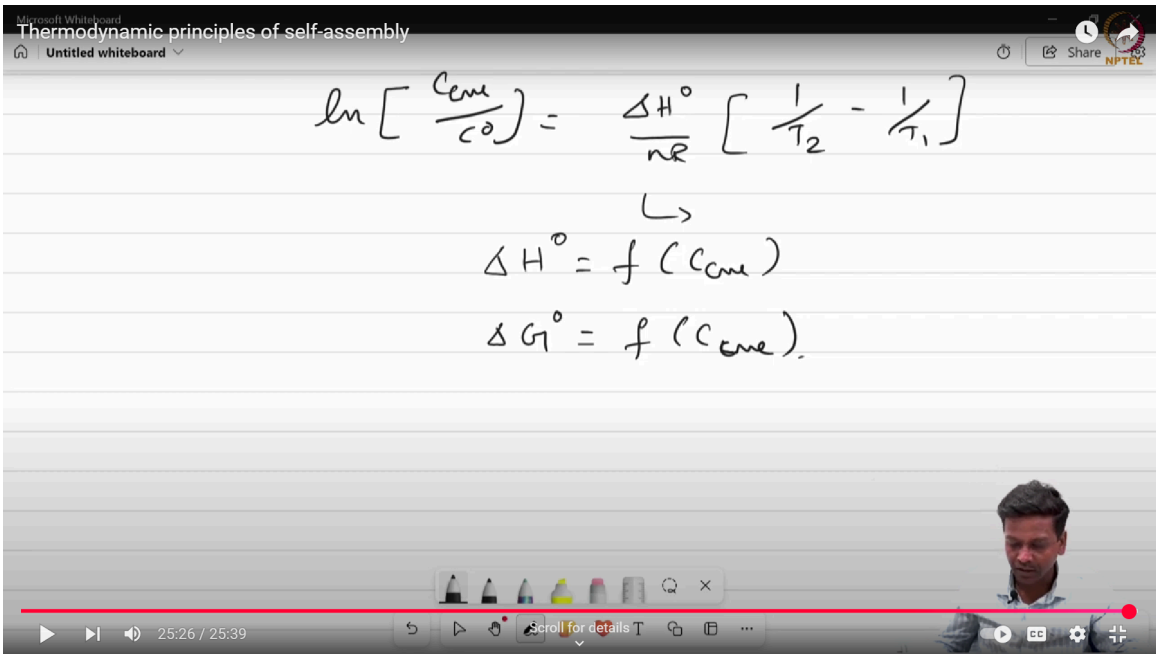

If we integrate both sides of the equation, we get: $nRln\frac{C_{CMC}}{C_0} = \Delta H^0\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

We can also express this as: $ln\frac{C_{CMC}}{C_0} = \frac{\Delta H^0}{nR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

This equation represents the enthalpy of micellization. Here, if we know the critical micellar concentration (CMC) and the concentration at the pure reference state, we can calculate the change in enthalpy at the standard reference state. The equation is in the form of a function of CMC, which aligns with our objective.

Now, we have derived equations for both cases: the Gibbs free energy and enthalpy are functions of CMC. If we have a binary mixture, we can calculate the change in Gibbs free energy at any pure reference state for the surfactant mixture or solution using this approach. We will stop here and continue from the next lecture.

Thank you.