

## **Interfacial Engineering**

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**Lecture-20**

**Surface excess concepts and problem solving**

**Surface excess; Gibbs dividing plane; adsorption at the interface**

Welcome back. So, in today's video lecture, we will try to look at the concepts of surface excess, right? And Gibbs dividing plane. And we will also look at the different types of surface excess and their consequences, right? And for example, positive surface excess, negative surface excess. We will try to, you know, talk about, you know, what are the, you know, implications of the Gibbs dividing plane. Okay. And we will see after that, we will see, we will try to solve one problem in the tutorial. Okay.

Let us begin. Right,

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Microsoft Whiteboard  
Surface excess concepts and problem solving  
Untitled whiteboard

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$\Gamma \rightarrow \text{gamma} \Rightarrow \frac{N}{A} \rightarrow \text{Interfacial area}$

+ve surface excess }  
-ve surface excess }  $\rightarrow$

Surfactant

2:59 / 31:19

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When we talk about surface excess, it is often denoted using a Greek letter, but that is  $\Gamma$ . So when we say surface excess, you can also alternatively call it as  $\Gamma$ . Surface concentration, which is nothing but  $N/A$ , right? Which is different from the concentration that we usually refer to, that is  $N/V$ , okay? So here, what is this  $N$ ?  $N$  refers to the number of atoms or molecules at the interface. And  $A$ , this is nothing but an interfacial area. Now, we will look at basically what is meant by the positive surface. There are two types of surface excess. One is the positive surface excess and the other one is negative surface excess. We look at the implications of these surface excess. Let's first understand what is the positive excess. Let's say you have got a B curve and you want to add some solute molecule like surfactant.

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The screenshot shows a whiteboard interface with the title "Surface excess concepts and problem solving". On the left, a diagram depicts a rectangular container with a horizontal line representing the liquid surface. Three small circles representing surfactant molecules are drawn along this surface, with arrows pointing towards it. The word "Surfactant" is written in red next to the diagram. To the right, a graph plots surface tension ( $\gamma$ ) on the vertical axis against concentration ( $C_{sur}$ ) on the horizontal axis. A red line with a negative slope is drawn, labeled "fres". At the bottom of the whiteboard, there is a video player interface with a progress bar at 3:54 / 31:19 and a small video feed of a man in the bottom right corner.

So as soon as we add the surfactant into the, you know, medium, what will happen is the surfactant has got a tendency to go to the interface and absorb at the interface, like something like this. So let's say they'll go to the interface and absorb the interface, right? Okay. So what will happen is as a function of concentration, let's say if I have to measure some interfacial property, let's say some surface tension, as a function of concentration, you will get the slope, you know negative slope right the slope that is negative okay because as a function of concentration surface tension decreases in this case because the surfactant has a tendency to go to the interface as soon as they reaches and absorbs at the interface they will reducing the surface tension.

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Surface excess concepts and problem solving  
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$$\Gamma = - \left( \frac{d\gamma}{dc} \right) \times$$

$\Gamma = +ve$  ✓ +ve surface excess

5:34 / 31:19  
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Now, our equation is related to the surface excess, which we will explore in the next lecture when deriving the Gibbs adsorption isotherm. This equation is a function of  $d\Gamma/dc$  (the derivative of surface tension with respect to concentration), multiplied by another term that we will discuss during the derivation. However, this equation will include a **negative sign**. When you substitute this negative slope into the equation, you ultimately obtain a **positive surface excess**.

In contrast, for inorganic solutes like NaCl mixtures, the behavior differs. If you measure the surface tension (denoted as  $\Gamma$ ) as a function of concentration, you would observe  $\Gamma$  increasing with concentration. For example, if the reference surface tension of pure water is 72 millinewton per meter, adding NaCl to water causes  $\Gamma$  to rise slightly as the salt concentration increases.

Right.

Timestamp: 5.34mins

The screenshot shows a whiteboard with the following content:

- A diagram of a rectangular container labeled "NaCl" representing a solution.
- A graph with surface tension on the y-axis and concentration on the x-axis. A red line shows a positive linear slope, labeled with a handwritten  $\gamma$  and "From  $\gamma$ ".
- Handwritten text below the graph:  $\Gamma = -ve$  and  $-ve$  Surface excess.
- A diagram below the graph showing a horizontal line with several small circles (representing water molecules) clustered below it, with a downward arrow pointing to the interface.

So why is this behavior observed? Right. So in this case, the surface tension increases as a function of concentration because this is a positive slope. Right. When you plug in this value into the equation, you will get a negative value ultimately. So which is nothing but negative surface excess. Okay. So, you might wonder why this is happening, right? First of all, when you add NaCl, the chlorine atom especially will have a greater affinity towards the hydrogen atom. So, what will happen is this NaCl molecule in the bulk will create some sort of a cascading effect with the water molecule, which means that there will be a water molecule in the vicinity of the interface, right? Because of the affinity between chlorine and hydrogen atom. So, this molecule will be pulled towards the NaCl in the bulk right further. So, as a result of which one can expect an increase in the surface tension right. So, as we stuff more NaCl salt into the equation this will attract right more water molecules in the vicinity of the surface. So, you will see that because these water molecules are now pulled towards the NaCl, it creates some sort of a cascading effect, okay, or crowding effect, right? So that will cause an increase in the surface tension as a function of concentration.

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Microsoft Whiteboard  
Surface excess concepts and problem solving  
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8:14 / 31:19

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So that's why this, you know, the solute molecule will, you know, lead to the negative surface excess, right? Right. So, now we have seen the positive and negative surface excess. Now, what is the consequence of this, right? So, the consequence of this is, let us say we are dealing with, let us say we are talking about, you know, immiscible mixture. We have one phase which is hexane. And we have another phase which is water.

This you can call it as alpha phase. And the water, the sub phase, you can call it as the beta phase. Let's say I'm now adding some X amount of surfactant type A and adding Y amount of surfactant type B.

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Surface excess concepts and problem solving

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$\beta$   $N = x + y$

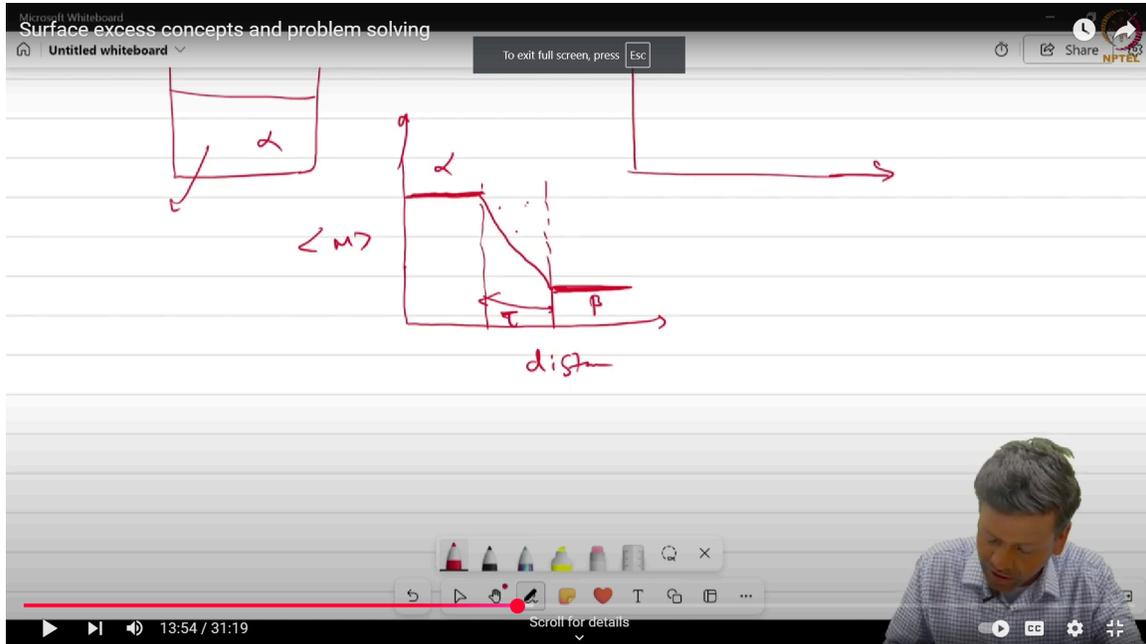
$N_A < N$

9:34 / 31:19

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Now, you might wonder what is going to be my total, you know, number of, you know, the surfactants that are present in the solution. So, that is nothing but X plus Y, right? But this is actually, this is our expectation, right? So intuitively, our intuition will say that this is additive, right? But that is not the case. So, when you measure with the actual number of moles will be slight, you know, lesser than the expected number of moles it is because some surfactant molecules present in the bulk okay, they have you know greater tendency to go to the interface and adsorb, when they get adsorbed some amount of the surfactant molecule go to the interface and adsorb. So, some of them are not available for the measurement, right? So, since some of them have gone to the interface when you measure the bulk, they will not be available for the measurement. So, which will lead to, you know, change in the number of moles that, you know, that, you know, one expects, right? One, you know, that we usually expect right it violates the conservation of mass in this case right it's because they tend to go to the interface where these surfactant molecules will not be available so this is one consequence. Similarly, you can also understand negative consequences when you measure the surfactant molecules in the bulk when you talk about the negative surface excess.

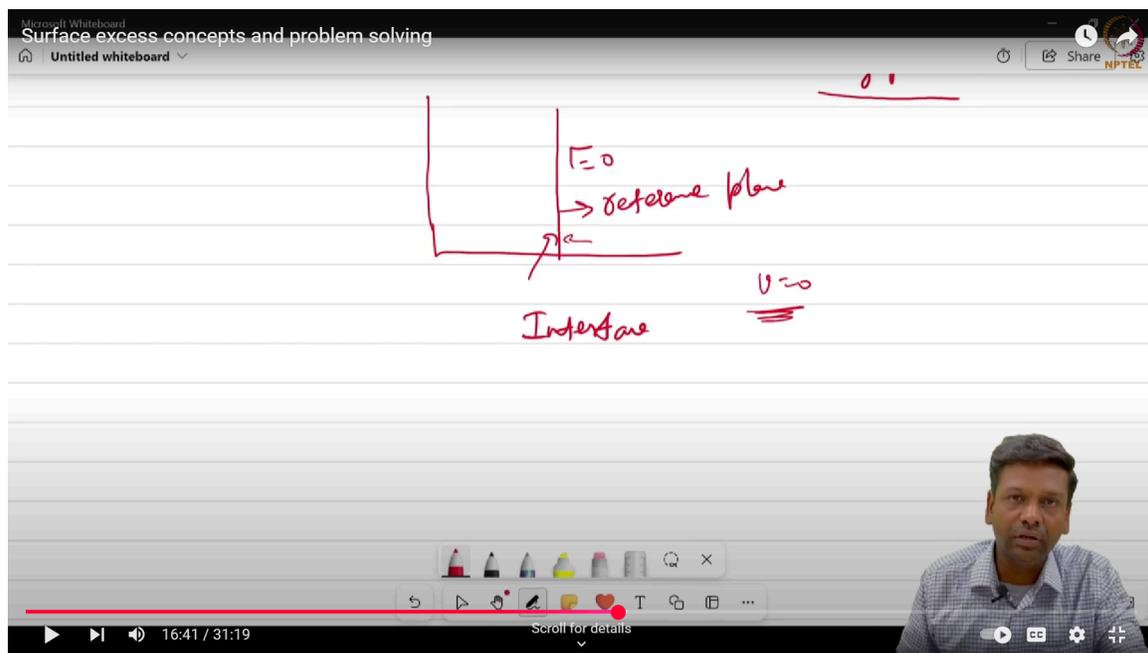
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Now what we will do is we'll understand something about the interface more in detail. Let's say, we perform some measurement using some probe, right? And we use this probe to move across the interface and try to understand or measure the property in both the phases, right? From both the phases, right? So now, let's say I have the, you know, container in which I've got two phases. One is an alpha phase. Another one is a beta phase. Now I'm going to introduce some sort of a probe, right? I'm going to introduce some sort of a probe. This will measure some property in the bulk and adjoining phases, right? So, if I do that, I understand that. So, let's say I measure some property, some average property, right? As a function of distance, right? As a function of distance across the interface, right? So, you expect that the property in the bulk because you know let us say we are measuring surface tension in the property in the bulk it will have some you know constant value. Similarly, this is the alpha phase similar way in the bulk which is the beta phase it will have the value same in the I mean throughout the bulk right because you understand that there will be the alpha phase is a homogeneous phase beta is itself a homogeneous phase right separately or individually so when you measure the property will be same throughout this phase but in between these two phase near the interface there will be a fluctuation Because the distribution of the molecules or atoms near the interface will drastically differ. In such a case, you would expect a change in the profile. It can be sometimes linear. it can be exponential or it can be any profile right so maybe for brevity you can understand that it is linear in this case you can say for sure that the property you know near the interface changes drastically. So based on this measurement, let's say the distance that is covered by this probe is the  $\tau$ . Now, if you want to understand what constitutes the interface and where exactly this interface lies, for example, whether the interface lies somewhere here or somewhere here or somewhere here because we

know that near the interface, the values are changing. But where exactly this interface this thin layer exists right lies that we don't know it is very difficult to you know locate that right. So, for that, what Gibbs proposed is that there is something called dividing plane okay. There is something called a dividing plane. So, Gibbs uses this use this dividing plane, you know, as a reference plane. Say, for example, you have the, you know. So, something if you choose a plane, this is nothing but a reference plane. In this reference plane, my surface excess is zero. So, if you choose a reference plane such that your surface excess is zero, then you can relate this reference plane as the interface, right?

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So remember when you look at the interfacial boundary although it appears I mean one can visualize the interfacial boundary through the naked eye in the actual sense the thickness of the interfacial zone or boundary is a few nanometers you know dimensions right sometimes Amstrom or sometimes nanometer in dimension so since it's very very thin layer right mathematically, we can you know refer to that plane as you know plane in which the volume doesn't exist right mathematically the volume doesn't exist so  $v$  is equal to zero in that case it's a fragile plane so mathematically there is no such boundary but although it exists right it exists in reality right so one can refer that plane as a as a reference plane with volume it occupies no volume. So, this is the Gibbs dividing plane also called the reference plane. So, this you can locate, name it as  $X_0$ . So  $X_0$  is the distance. Right.  $X_0$  is the reference plane. OK. Right. So what is the advantage of this? Say, for example, whenever you deal with, let's say, a binary mixture.

Whenever you deal with the binary mixture, usually one would have, you know, solvent. And the surfactant. Solvent and the surfactant.

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The screenshot shows a Microsoft Whiteboard interface with the title "Surface excess concepts and problem solving". The whiteboard content includes the word "Interface" at the top, followed by "Binary mixture" and "Solvent + Surfactant" with an arrow pointing to a diagram. The diagram depicts a vertical line representing the interface, with a horizontal line above it representing the surface. A vertical line is drawn through the interface, and a horizontal line is drawn through the surface. The intersection of these lines is labeled "Gamma = 0". The region below the interface is labeled "x\_0". The whiteboard also shows a toolbar with various drawing tools and a video player interface at the bottom with a timestamp of 18:37 / 31:19.

So, if you choose the dividing plane for solvent usually solvent molecules do not have any tendency to adsorb at the interface right. So usually, the solvent will exhibit a profile you know in a very symmetrical way okay. Usually, the solvent will exhibit a profile in a very symmetric way because they do not have any tendency to adsorb by the interface. So, in this case, you can choose the you know this surface excess such that you know when you divide this into two halves. When you divide this into two exactly at this point, the gamma equal to zero. Because, you know, this is this side and this side. When you measure, there will be an equal number of surface excess.

So, you can say that at this point, my interface exists. So, at this point, my interface exists. So, I can say that surface excess is zero. Now when you say surface excess is zero at this point so there is only one component left which is the surface excess of the solute molecule right surface excess of the solute molecule that is surfactant in this case. So, it is easier for us when you have the equation for surface excess, especially for binary.

One of the surface excess components we can denote, I mean we can neglect because we choose the dividing plane such that the surface excess is zero. It will be clearer when we show the presentation so that you will understand better.

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Microsoft Whiteboard  
Surface excess concepts and problem solving  
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So, the idea of this dividing plane is one cannot easily locate the interfacial, you know, point. So to do that, one has to choose the reference plane such that, you know, you can achieve, I mean, you can make the, you can divide the point the distribution the profile the distribution into two equal of so that the midpoint is exactly where the interface lies right. So, you can say that that is nothing but your dividing plane ok?

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Surface excess concepts and problem solving  
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$$V = V^\alpha + V^\beta + V^{\text{int}}$$

$$N_i^\alpha = N_i^{\text{total}} - N_i^\beta - N_i^{\text{int}}$$

$$= N_i^{\text{total}} - c_i^\alpha (V - V^\beta) - c_i^\beta V$$

21:02 / 31:19

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The idea is to use the reference plane to define the surface excess of the solvent molecule as zero. This allows us to establish a mathematical framework for surface excess calculations.

We start with the total volume  $V$ , which consists of three components:

$$V = V^\alpha + V^\beta + V^\sigma$$

where  $V^\alpha$  and  $V^\beta$  represent the bulk phases, and  $V^\sigma$  accounts for the interface. However, mathematically, the interface volume  $V^\sigma$  is considered zero, meaning the dividing plane helps us eliminate  $V^\sigma$  from the equation.

Now, to determine the surface excess of a given solute ( $\Gamma_i$ ), we define  $n_i^\alpha$  as the number of species of component  $i$  present in phase  $\alpha$ . Using a component balance, we express the total number of species ( $n_{i\_total}$ ) as:

$$N_{i\_total} = N_i^\alpha + N_i^\beta + N_i^\sigma$$

Since the interface contribution  $n_i^\sigma$  is what we define as surface excess, we rearrange the equation as:

$$\Gamma_i = n_{i\_total} - N_i^\alpha - N_i^\beta$$

Substituting for  $n_i^\alpha$  and  $n_i^\beta$  using their respective concentrations:

$$\Gamma_i = N_{i\_total} - (C_i^\alpha V^\alpha) - (C_i^\beta V^\beta)$$

where  $C_i^\alpha$  and  $C_i^\beta$  are the concentrations of species  $i$  in phases  $\alpha$  and  $\beta$ , respectively.

This expression allows us to compute the surface excess of a given solute using the reference plane approach. Now, we can further refine this equation based on specific system parameters.

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Surface excess concepts and problem solving  
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$$N_i^\sigma = N_i^{\text{total}} + V^\beta [C_i^\alpha - C_i^\beta] - C_i^\alpha V$$

$$\frac{N_i^\sigma}{A} = \frac{N_i^{\text{total}} + V^\beta [C_i^\alpha - C_i^\beta] - C_i^\alpha V}{A}$$

$\hookrightarrow \Gamma_i \rightarrow$  surface conc

22:22 / 31:19  
Scroll for details

We can rewrite  $V^\alpha$  as:

$$V^\alpha = V - V^\beta - C_i^\beta V^\beta$$

Rearranging this, we can express it in terms of the total number of species:

$$N_i^{\text{total}} = V^\beta (C_i^\alpha - C_i^\beta) - C_i^\alpha V$$

where  $V^\beta$  is common in the first term. Now, dividing both sides by the interfacial area  $A$ , we obtain:

$$(N_i^\sigma / A) = (N_i^{\text{total}} V^\beta (C_i^\alpha - C_i^\beta) - C_i^\alpha V) / A$$

Here,  $N_i^\sigma / A$  represents  $\Gamma_i$ , the surface excess of species  $i$  at the interface.

Thus, we conclude:

$$\Gamma_i = N_i^\sigma / A$$

Where  $\alpha$  and  $\beta$  represent the two adjoining bulk phases, and  $\sigma$  refers to the interface.

All right.

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Surface excess concepts and problem solving: Thermodynamics of interfaces

(-) Surface excess      (+) Surface excess

Adsorption      Equilibrium      Desorption

$\Gamma < \Gamma_0$        $\Gamma = \Gamma_0$        $\Gamma > \Gamma_0$

surface expansion      surface contraction

monomer transport      monomer transport

J. Eastoe, J.S. Dalton, *Advances in Colloid and Interface Science* 85 (2000) 103-144

Adsorption of the surfactants from solution

A. Ch. Mitropoulos, *Journal of Engineering Science and Technology Research* 1-3

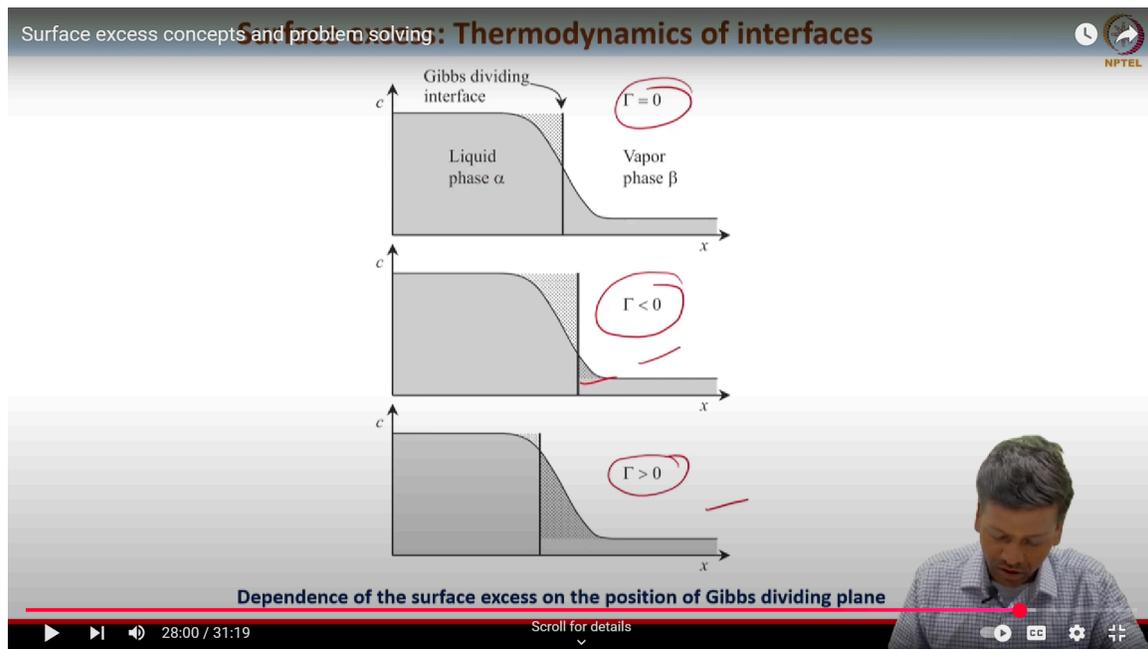
► Presence of an interface influences all thermodynamic parameters of a system.

26:27 / 31:19      Scroll for details

It will be clearer when we look at the presentation that we have. This is nothing but the surface excess, right? So, you can see the profile of the surface axis for solvent, this is for solvent molecule, and this is for solute molecule. For solute molecules, because surfactants have got adsorbing tendency, there will be one I mean, it is not always possible that we expect a symmetrical distribution or symmetrical profile, whereas in the case of solvent, because they don't have any adsorbing tendency, you will expect a symmetrical distribution, right? So, this will make us identify, right? A midpoint such that the surface excess you know left and right both the side when you sum up they will be this side it is all negative this side it is all positive so both will be equal to zero right whereas in this case because they are asymmetrical the distribution is asymmetrical, you will not be able to get you to know equal of so solute here will be very difficult to identify what is a midpoint or what is the reference plane right but here it is very easy to understand the reference plane because at this point you got a midpoint where the gamma here the excess gamma excess is zero right. So, when you identify the midpoint, it is easy for us to calculate the, or to say that, so whenever you deal with the binary mixture, let's say, it is easy for us to ignore one of the components. Let's say for solvent, you can ignore it easily. To say that, by saying that, when you, at this midpoint, or this dividing, when you use this as a dividing plane. At this point, the surface excess for solvent is zero. Based on that, you can calculate the surface excess for the solute, right? So, that is the idea, right? This is all about the Gibbs dividing plane. Now, let us say we are talking about surface excess and positive and negative surface excess and equilibrium, right? Surface excess, okay. So, what is the direction of the transport of the solute molecules is something that we need to understand. If you look at the adsorption surface negative if

the number of molecules right the molecules at the interface if the concentration of a surface excess of the molecule at the interface is less than the equilibrium surface tension then you would expect the monomer transport the direction of the monomer transport will occur from the bulk to the interface the direction of the movement of the molecule will be from the bulk to interface until they attain equilibrium right at the equilibrium because they have already reached the equilibrium there will be no net movement between bulk and interface in this case right whereas in the case of the positive surface excess if the surface excess is more than the equilibrium in that case because it's a positive surface excess so you will you will have more number of atoms than the equilibrium concentration you would expect that there will be a desorption right you can expect that there will be desorption so monomer will usually travel from the diffuse from the interface to the bulb right so these are based on the equilibrium surface excess concept.

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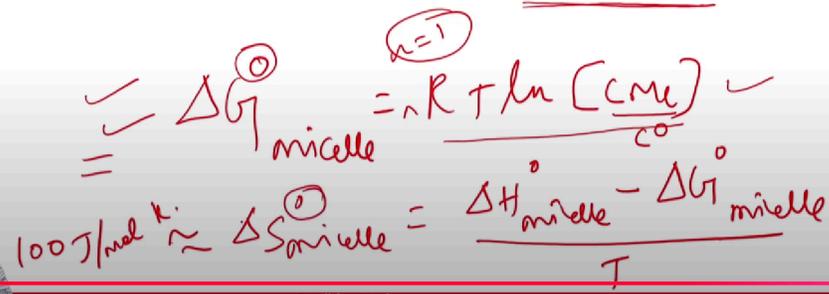
Now you can see what is the consequence of the dividing plane. If we choose a different dividing plane, how the surface excess is changing, right? The nature of surface excess is changing. If you see that exactly when you choose a dividing plane such as that, you found a midpoint and at this point reference plane gamma is zero right, in this case, the gamma I mean this this gamma is zero whereas here if we choose the reference plane slightly towards the right closer to you know the adjoining bulk phase you would expect that the surface excess will be less than zero, in this case, okay you would expect negative surface excess in this case if you choose the dividing plane little further from you know from the midpoint towards left you would expect the surface excess positive surface excess in this case so this will you know lead to some you know setback right

because we are not able to identify you know a proper you know we are not able to choose the reference plane in the appropriate way.

Timestamp: 28 mins

Surface excess concepts and problem solving **Tutorial** 

At 25°C, the CMC for CTAB is 1 mM in water. An analysis of the temperature variation of the CMC gives  $\Delta H_{Mic}^0 = 2.51 \text{ KJ/mol}$ . Evaluate  $\Delta G_{Mic}^0$ , and  $\Delta S_{Mic}^0$  from these data. Omit counterion binding by taking  $m = 0$ . Comment whether the process of micellization is spontaneous or not. Data: You can take concentration of pure water (std. reference state) as 55.5 mol/litre.



31:08 / 31:19 Scroll for details

Now we'll see a tutorial based on the CMC, critical micellar concentration, which we have seen in previous lectures. When we try to derive the change in Gibbs free energy for, for micelle so in when we derived the changing Gibbs free energy of micellization we know that this equation exists right. This equation we saw we derived when we dealt with you know micellization right so in this equation you know what is to be known is the critical micellar concentration that is cmc right for the case of ctap that is the ctap surfactant the concentration cmc of that is given one millimolar in water that is already given temperature data is given. They have given also you know change in enthalpy of micellization at standard reference state. So, what is being asked is to calculate the delta G micellization at standard reference state and entropy, change in entropy of micellization at standard reference state. That is, we need to evaluate these two, you know, unknown, right? So, we know that if you want to calculate the Gibbs free energy of micellization at standard reference state, this is the formula because we use the, you know, this is in since we use this capital G here, you can assume that n here is 1, right? So, it's supposed to be nRT. You can assume n to be 1 in this case, right? So we know that, so whenever you evaluate the CMC, you have to evaluate concerning some standard reference state. In this case, it is a pure water, okay? You can assume, you can take this value as such. So, considering that the standard reference state is pure water, the right is 55.5 moles per liter. So, when you substitute this, you would get the value for delta G micellization at constant reference, standard reference state will be minus -27.056 kJ/mol.

Now when you substitute this into this equation because  $\Delta H_{\text{micelle}}$  is also given. So in this case your  $\Delta S_{\text{micellization}}$  will be approximately  $100\text{J/molK}$ .

Right. So, in this way, you can calculate what is the change in Gibbs free energy of micellization at the standard reference state. And, you know,  $\Delta G$ , since in this problem,  $\Delta H$  is given, you can also calculate the change in entropy of micellization at standard reference state.

We stop here.