Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 27

Surfaces and interfaces

So, in lecture 9, part 1, we discussed about the applications of the equilibrium thermodynamics in electrochemistry, where we discussed about the electro motive force and how it is connected to the changes in Gibbs free energy and then we also talked about the Nernst equation and we talked about the cell potential in that lecture. So, in today’s lecture, we will be discussing about another application of thermodynamics or equilibrium thermodynamics, which are applications to of surfaces and interfaces.

Now, surfaces and interfaces are extremely important and particularly in terms of say catalysis, which we will be discussing in under chemical kinetics portion, and there we will see how basically, the presence of a surface can lead to the adsorption of one particular reactant or many reactants together, and then how they help in breaking or the particular bonds in the molecule, and thereby providing the necessary energy of activation and our lowering the energy of activation of the energy barrier that the reactants would have required, if that we perform the reaction in gas phase.

So, the presence of surface dramatically modulates the rates of reaction, but in today's lecture we will be discussing only on the thermodynamic aspects or the equilibrium aspects. How the surface actually changes the thermodynamics? How it is different from the bulk phase, that we will discuss today. Now, to begin with, you can think of a system with an interface.

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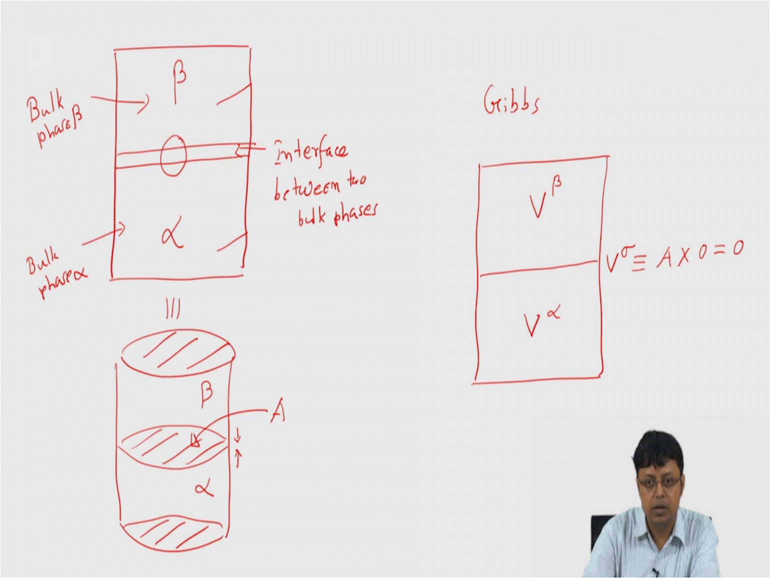

And when you talk about interface, it must consist of two bulk phases suppose, these bulk phases I am writing as alpha and beta and then there is an interface. So, this is one bulk phase say, we call it as a bulk phase beta and similarly, this is a bulk phase alpha and this one, we call it as an interface. So, this interface is between alpha and beta. So, it is between two bulk phases.

Now, the question is how we model this interface? Now, to begin with let us try to understand, what is the thickness of this interface? Now, you can think that this interface is actually of very thin dimension. The way I have drawn, it is actually to some extent, not to some extent. It is highly exaggerated, because if you think that this alpha and beta are non-electrolyte, then you will see that this interface will be a few molecular thick.

So, you can actually do a good approximation, think that this interface has 0 thicknesses; however, it will have an area, because if you remember that the way we are drawing it on these 2 d surface, do not forget that it is something like a cylinder. It is a cylindrical system. So, it has an area, the interface has an area and each this is alpha phase. This is beta phase, but now, we are talking about fine.

There is an area of the interface, but does it have any thickness and this thickness you can ignore it and that model was provided by Willard Gibbs, where he considered that well. We will consider interface to have some area of course, but with 0 thickness, which means the volume of the interface will also be 0.

Now, this will be very important. So, this volume of the alpha phase, we call it as a V alpha, the volume of the beta phase, we call as V beta, but volume of the interface, which we denote as sigma V, sigma is nothing, but 0, because the thickness is 0. So, it is nothing, but the area times, the thickness which is 0 and that is why it is 0. Now, we will be discussing the thermodynamic properties of this interface. Now, before going into detail let us try to understand how the energetics of the interface should be compared to the bulk phase.

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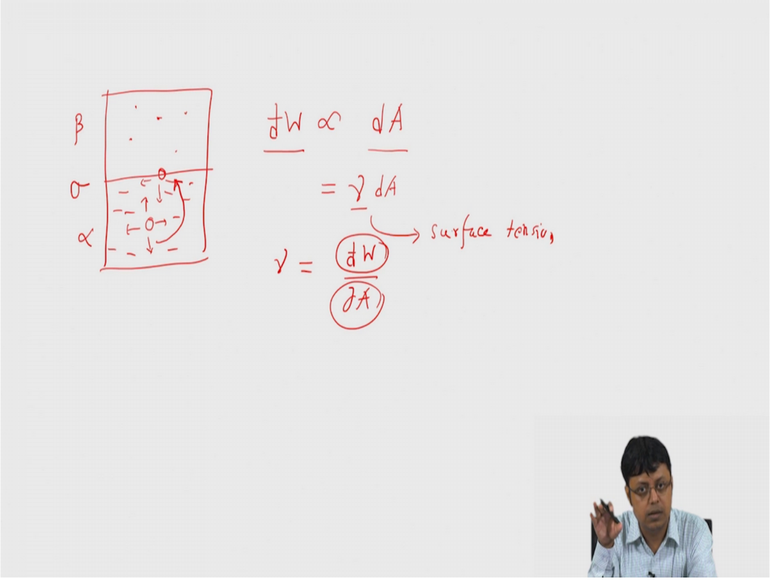

Suppose, there is a molecule in the alpha phase, and when it is in the bulk or inside the alpha phase, it is being attracted or there are some kind of interaction and this interaction, the molecule fills from all sites and to an good approximation, we can think that the isotropic nature of the medium. So, you can think all these interactions actually averaged out. So, the molecule actually experiences. Now, net force on its motion; however, when you bring the molecule on a surface.

So, suppose this is just a liquid, suppose this is water and we are bringing one water molecule or one say, some molecule is dissolved in water and you are bringing that molecule to the surface and then you will see that fine. This molecule is having interaction with water molecules in all side, but in the surface there are a very less number in molecules, in the beta phase, because there will be some water molecules a very less number in the vapor phase.

If we carry out this in a cell tube; so, it will have an unbalanced force, the molecule will experience an unbalanced force, which means in order to bring the molecule from the bulk to the surface, we have to do some work and this work will be definitely proportional to the increase in the surface area, which is associated. Why there way increase? Because if we bring one particular molecule from the bulk to the surface, what effectively we are doing is that we are increasing the surface area. So, that will involve some work and this is positive work, because here actually, we are doing that work not the system, we are bringing, increasing the surface area of the system and that is why the surrounding is doing some work and that proportionality constant. We call it as gamma, where gamma is known as surface tension.

So, the surface tension can be defined as the work done per unit change in area. So, that is the definition of surface tension. So, it will have dimensions of energy per square centimeter or square meters something like that. Now, think about it, for this what we have talked about the surfaces or interfaces. We have to choose a particular molecule or particular component and discuss about its thermodynamic properties in phases alpha or phase beta, and at the interface, which we denoted as sigma.

Now, what do you mean by that? Think about it, like say for example, we add some salt in water now, the question we are asking, whether this salt will preferentially stay in the alpha phase, which is the liquid water phase or in the beta phase, which is actually the water vapor phase or it will stay, it preferentially in between the sigma or the surface region.

Now, for salt actually we will see that, it will preferentially, would like to go into the bulk phase, but there will be, there are many other molecules that will preferentially you would like to stay in the surface. Now, how do you quantify it? That is the first question. Now, for that let us assume that we are plotting the concentration of a substance as we cross the alpha to the beta phase.

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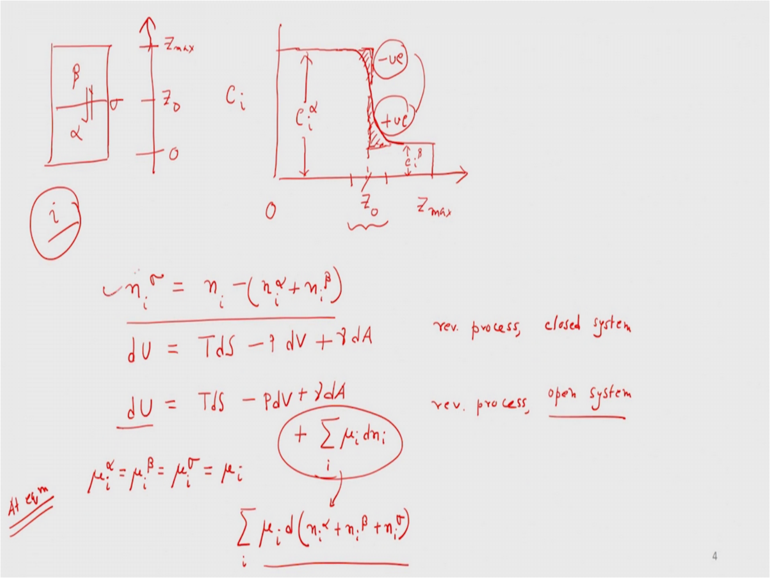

$$n_i^{\sigma} = n_i - (n_i^{\alpha} + n_i^{\beta})$$

$$dU = TdS - PdV + \gamma dA$$ rev. process, closed system

$$dU = TdS - PdV + \gamma dA \boxed{+ \sum_i \mu_i dn_i}$$ rev. process, open system

At eqm

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\sigma} = \mu_i$$

$$\sum_i \mu_i d(n_i^{\alpha} + n_i^{\beta} + n_i^{\sigma})$$

Suppose this is alpha, this is beta and of course, this is sigma and suppose, along this direction we are varying, we are basically watching, how the concentration varies and let us also say that at this point, we call it as a Z equal to 0 and the dimension of the system or the length of the system in this Z direction is say B, it is some parameter and at or we can actually call it as say something in terms of Z say we call it as a Z max and then at the midpoint, where the interface exists, we call it as Z 0.

Now, I am plotting the concentration of some species say I am calling this species as i. So, I am plotting Ci and how it is varying, if I vary the Z from 0 to say Z max. Now, since concentration is an intensive property, it should not change, I mean it should be a flat line f, if we go within as phase and then we may see very interesting phenomena. So, here the concentration corresponds to the alpha phase, I am writing it as Ci alpha and suppose, the concentration drops in beta phase. So, I am calling it as Ci beta and then the question is how does it drop? Does it drop abruptly?

The way I have drawn by that dotted line, if it does abruptly then actually it is just the alpha phase and the beta phase. There is no interface in between, but in reality what happens? You will see the concentration will slowly change like this, it will drop slowly and it will go like this. So, what you discover here is that the concentration. Here, in the alpha phase, where this distance is just say the Z 0, distance actually start dropping much before the Z 0 is attent. It is not actually much before, I mean we are again exaggerating, the thickness of the interface here, but the point here is that, it starts dropping before, it has reached the length has reached Z 0. So, it starts dropping and then it also starts, it is little bit higher also before it, after even after it has crosses Z 0.

So, you see here that, the concentration should have been like this for the alpha phase, but it has drop. So, this area corresponds to a negative area as if the concentration is has dropped from its bulk phase concentration. Similarly, here you can see the concentration has actually increased, compared to its bulk area.

So, what you can see here, if we multiply this drop and the increase and addition basically and subtraction of this concentration and first you add these two values of how the concentrations are changing and then, if you can multiply it with the thickness of these interface and times the area, then you get the volume of that interface and then you can ask this question whether, these two area, the positive area and the negative area, do the perfectly cancel.

If they are perfectly cancel out, then it means that the interface does not have any excess number of molecules; however, you may get a situation that the positive area is more than the negative area, which means in the interface, you will get a net excess of molecules, compared to the alpha phase or the beta phase. It is the way you have drawn it, and on the other hand, you make it overall negative area, which means actually the concentration of the molecules in the interface real region are actually less. So, based on that, we will see that, we can divide the molecules into different types. Now, the question is how you will do? How you will formulate the thermodynamics of this problem.

Now, to begin with we will just do the mass balance in the sense that, we know that the total number of molecules in the interfacial region for the i th spaces that will be nothing, but the total number of molecules minus the number of molecules in the alpha phase plus the number of molecules in the beta phase that, would be always true. Now, next thing is that, we will start from the first law of thermodynamics and for a reversible process. We can write it as the d cross q term at Tds and then we can write it. There will be some pressure volume work and plus there will be some work, which is also associated due to the increase or decrease of the surface area that we wrote as gamma into d A.

Now, this is for a reversible system of course, our reversible process, and this is also for a closed system the way you have drawn it or we have written it; however, you if you think that this component i, this is actually freely transferring between the alpha and the beta phase; so because there is a gradient in concentration from going from alpha to the beta, through the interface. So, we have to add some additional term, for the reason is, this system is an actually open system, because we see exchange of mass across the interface. So, the first law in the first, all we have to consider, if you remember our discussion on chemical potential.

This P is actually capital P plus gamma dA plus the way we write it all the additional term, due to the change of number of moles from one phase to the other phase that we can write it as sum over mu i dn i. So, that we already discussed, when we discussed the Gibbs free energy per unit mole or the chemical potential. So, where mu i is the chemical potential at the i th spaces. Now, this is also for a reversible process, but now, we have made it more general, we are considering for an open system, where we added this extra term. Now, the question is how you write this extra term?

Let us just try to have a look. So, we know that what is mu i dni. So, if you ask this question, what is mu i dn i? So, mu i will be the chemical potential, but do you know that is chemical potential of which phase we have to define that now at equilibrium. You can approximate that not approximately; when the equilibrium has at each attent, you can always say that the chemical potential of a particular constituent, which we are denoting as i here, will be same in all the phases.

So, mu i of alpha will be equal to mu i of beta will be equal to mu i of sigma, which means now, we can just write it as something like mu i. Now, this term; now, we can expand it as if it is sum over i mu i. Now, d of ni, but we already know that n is nothing, but ni alpha plus ni beta plus ni sigma. So, we can just write it like this n i alpha plus n i beta plus n i sigma, where alpha and beta are for the bulk phases and sigma is denotes for the interface.

So, what we get is a very interesting situation. Now, what we are going to do is that we are going to write the different terms. Different, I mean different terms, in the sense that this d U is nothing, but we know that we can write it as the total U or the internal energy also as the energy of the alpha phase plus beta phase plus gamma phase, just the same way we have written the number of moles for the alpha phase, beta phase, or gamma phase.

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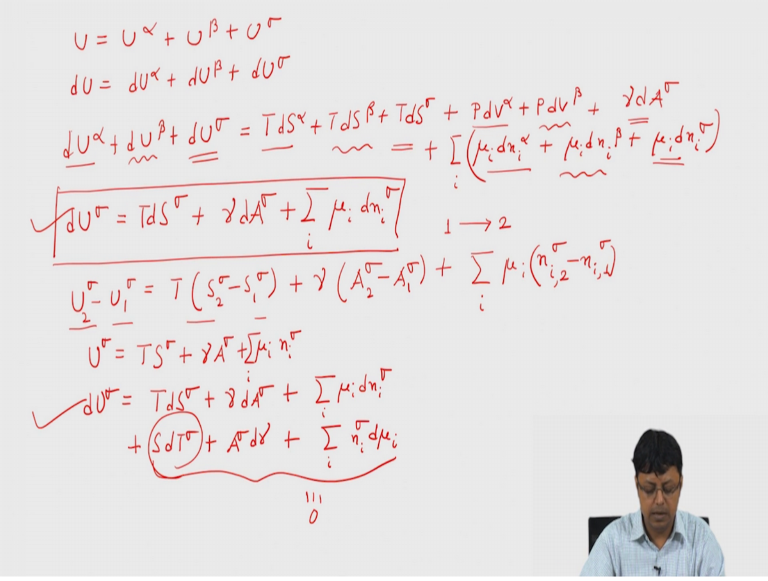

$$U = U^{\alpha} + U^{\beta} + U^{\sigma}$$

$$dU = dU^{\alpha} + dU^{\beta} + dU^{\sigma}$$

$$dU^{\alpha} + dU^{\beta} + dU^{\sigma} = TdS^{\alpha} + TdS^{\beta} + TdS^{\sigma} + PdV^{\alpha} + PdV^{\beta} + \gamma dA^{\sigma} + \sum_i \left(\mu_i dn_i^{\alpha} + \mu_i dn_i^{\beta} + \mu_i dn_i^{\sigma}\right)$$

$$\checkmark\ \boxed{dU^{\sigma} = TdS^{\sigma} + \gamma dA^{\sigma} + \sum_i \mu_i dn_i^{\sigma}} \qquad 1 \longrightarrow 2$$

$$U_2^{\sigma} - U_1^{\sigma} = T\left(S_2^{\sigma} - S_1^{\sigma}\right) + \gamma\left(A_2^{\sigma} - A_1^{\sigma}\right) + \sum_i \mu_i\left(n_{i,2}^{\sigma} - n_{i,1}^{\sigma}\right)$$

$$U^{\sigma} = TS^{\sigma} + \gamma A^{\sigma} + \sum_i \mu_i n_i^{\sigma}$$

$$\checkmark\ dU^{\sigma} = TdS^{\sigma} + \gamma dA^{\sigma} + \sum_i \mu_i dn_i^{\sigma} + \underbrace{S dT^{\sigma} + A^{\sigma} d\gamma + \sum_i n_i^{\sigma} d\mu_i}_{\overset{\shortparallel}{0}}$$

So, in that way if you write it; so, what I am saying here is that, you could write it as U alpha plus U beta plus U sigma and then you could write it as d U is nothing, but d U alpha plus d U beta plus d U sigma. So, that way we can actually write all the terms and then you can ask this question that how these individual terms? For example, this d U or d S, they change. Now, let us rewrite it once again.

So, we are writing it, d U instead of d U I am writing as d U alpha plus d U beta plus d U sigma is equal to then we have Tds, we will have T d s alpha plus Tds beta plus T d s sigma plus there was a P d V term. So, I will have P d V alpha plus P d V beta, but there will be no P d V sigma, because the d V of sigma V of sigma is 0. So, there will be no pressure volume work associated for the interface, because the interface has 0 thickness and hence, 0 volume and then we have one term, which was a d gamma and remember that is only associated with the interface.

So, it is not associated with the bulk phases. So, that a d gamma term is very specific for the interface and then we have all the new terms, where we can write it as mu i dn i alpha plus mu i dn i beta plus mu i dn i sigma and that is only for one particular component for, if we have many components, then we have to take a summation over all these components. So, now, we can just equate term by terms. So, we will get one equation for the alpha phase, one equation for the beta phase like this and then we will also get one equation for the gamma phase and we are only interested in the equation, for the gamma phase, because we are only considering the thermodynamics of interfaces. So, we can write that d U sigma is nothing, but T d S sigma plus a remember that, there is no P d V term for the surface a sigma d gamma plus it will be sum over i mu i dn i sigma, because mu is are equal. So, I am not writing mu i sigma or mu i alpha or mu i beta. So, this is basically, the first law or the surface or the interface in this case.

Now, we can always integrate it, we can think that the system is going and undergoing a change from state 1 to state 2 and then if we integrate between these states, you will get nothing, but something like U 2 sigma minus U 1 sigma is equal to T of S 2 sigma minus S 1 sigma plus some area times, this d gamma or it should be actually gamma d A. So, if we go back one slide.

So, we see that it will be gamma d A, it is not a d gamma. So, you can correct for that. So, it will be a gamma into d A and that A is associated with some area. So, it will be gamma d A instead of A d gamma and then we can write it as the surface tension times A 2 of gamma minus A 1 of gamma naught gamma. It is sigma and then we have the sum over the terms, which are something like we can write as if we integrate in i 2 minus n i 1 and this is for the interface.

Now, what we can conclude from here, the internal energy for the interface can be written, you can see that this is basically, difference between the state functions. So, U is a state function. So, we can also write it, as internal energy is nothing, but TS sigma plus gamma A sigma plus mu i ni sigma and now, you can take again the total derivative and you know, how the total derivative is done.

So, you have to write T d S sigma plus there will be a second term, which will be S d T sigma. So, the same approach we also use to discuss the Gibbs Duhem equation, when he wrote the Gibbs free energy as mu i dni mu i and then integrated, it to get mu i ni and then again took the differential to get mu i dni plus ni d mu i and we said that that ni d mu i terms has to be 0 the same approach, you are going to do here.

So, we have here gamma d A and similarly, we will have A d gamma plus we will have some over i mu i dni sigma and here will have some of our i dni sorry, it will be ni sigma into d mu i. So, we can see by comparing this equation and this equation, which we just got that this part must be equal to 0. We can make a further approximation and we are going to make another approximation, where we will talk about only the isotherms or we basically, we are keeping the temperature constant, which means there now the S d T will also be 0. So, what we get from here is that we have A d gamma plus sum over the constituent i and written as n i sigma d mu i is 0.

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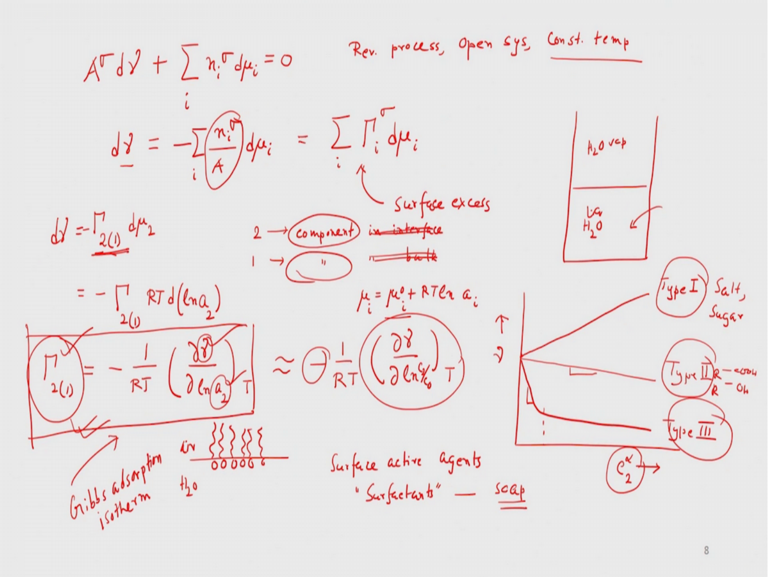

Now, we can rearrange it a little bit and we can get the value of d sigma, this is remember, this is for a reversible process and this is for an open system, because we have made it very general and also this is for open system and we also made it for constant temperature, because we have dropped the S d T term. So, d sigma or is d omega is nothing, but minus n i sigma divided by A into d mu i.

Now, remember what was n i sigma; ni sigma was the total number of moles minus the moles of, in the present, in the inter bulk phases like the alpha or the beta. Now, if you remember this particular curve, where we discussed about these positive and the negative areas, or the regions of the concentration; so, this concentration multiplied by the small thickness and then multiplied by the area will give you the number of moles.

So, those number of moles are actually will be excess, if this positive area is more than the negative area, it will be the other way around, if the negative area is more and it might be 0 also if these area to area perfectly cancels. So, what do we are asking right now, is that we have got an expression for gamma, which is surface tension connecting to the number of moles in the interface, which actually is corresponds to this excess number of moles, in the interface divided by area. So, we see a very beautiful relation here, that this quantity the number of moles or which is excess in the surface per unit area that we term as surface excess and we write it as gamma i sorry, it is gamma i and we call it as a surface excess. So, it will be nothing, but gamma i into d mu i sum over i.

So, we can now also say that this gamma i is nothing, but a property of the interface that is why I am keeping notation sigma there. So, now, we can actually plot the sigma versus the concentration, but before that, let us try to understand what is the sigma? So, we can for that, we can actually expand it little bit. So, suppose we have only one component.

So, I am writing it as 1, but we always write it as this, instead of writing it as gamma suffix 1, we always write it as component with respect to the bulk phase. So, 2 here denote that, how many molecules are there in the interface compared to the bulk phase. So, for example, to give you a filing that, I have an alpha phase say, it is water and then I have air here, where you can have water vapor and here, I have liquid water and then I am adding some salt and then I am asking how much excess I have.

So, it is basically, gamma 2 with respect to the 1 phase that we are writing for a particular component that 1 component. So, it will be minus d gamma mu 2 1 and times mu d mu 2, because the 2 we are writing it for the component, because there are some component of the particular thing, which are also in the liquid phase or in the bulk phase. So, these two is for component in interface.

So, that will tell us the surface excess. So, it is excess with respect to bulk that is why you were writing 2 and in parenthesis, we are writing as 1. So, it is with respect to the bulk and it is component in bulk phase. So, if you write it at the mu in terms of our, if we expand it in terms of the standard chemical potential, we know that it will be nothing, but mu is mu 0 plus RT ln activity of the spaces, if it is species, I will write it something like that.

So, if I take the derivative this problem will be 0, because mu 0 is nothing, but a standard state activity, standard state chemical potential, the derivative of which you will be 0. So, we are left with only RT ln activity of this particular component. So, we can write it as minus gamma 2 into RT ln and instead of taking the derivative; will just write it as d of RT ln Ai. So, what we get right now is this quantity gamma 2 1 will be nothing, but minus 1 over R T into del gamma del ln A 2 instead of i we can write it as A 2, because we are considering the activity of that component at the interface and that was taken at constant temperature. Now, for dilute solution we can approximate the activity to be equal to the concentration.

So, we can write it something like this d C omega d as d gamma and del gamma and del ln C 2 at constant temperature, it will not be actually C 2, it will be to be very precise, it will be C 2 by C 0 it has to be always d be divided by the standard state which is 1 mole correlated. Now, you see that if we plot the gamma versus T plot for and look at different substances, you will see for few substances. Actually, the slope will be positive, the positive slope means d del gamma del, ln slope is also positive. So, what you will get from here, it is not versus T, it is versus C 2 the concentration of the molecule in, say some phase, which is in say alpha phase. Now, what you see here is that we have an increase here and this increase or the molecules, which show this type of increase. We call it as a type 1 molecule.

Now, type 1 molecules means actually, there is a positive slope, which means actually, the gamma, the surface, excess will be negative, because there is a negative sign here. So, this molecules will preferentially would like to stay in the bulk, examples are something like a salt or say organic compounds like sugar, say for example, sucrose or glucose, they will preferentially would like to stay in water phase, because they are highly water soluble.

There are some compounds which actually show a slight negative trend, which we call as type 2, these are organic compounds with C oo H or alcohols, which actually have some hydrophilic part and those hydrophobic part would actually, would like to go into the air fest in the hydrophobic in the sense that ripple water, they actually do not ripple water. So, water interaction is more than the water and alkyl gel in interaction.

That is why; they prefer to stay away from water, but there this slope is not that much negative, in the sense that the gamma is not that much positive also. So, they preferentially accumulate in the interface, but not much. There they actually, stay both in the bulk phase as well as in the interface and then you will also have a third type of molecule, where you will see a large drop in that concentration, large top in that slope, which means actually, this is very highly negative. This slope which means gamma is highly positive and these molecules, which we call as type 3 molecules, which will show preferential accumulation in the interface and they are collectively called as surface active agents, because they are activating the surface as if they are increasing the surface area, because they are going into the surface more and more than in the bulk phase.

Surface active agents or in a short form, they are known as surfactants and the examples of surfactants are like; soap molecules. So, all these long chain fatty acid molecules which, for example, under salts like sodium stearate or sodium palmitate. They have a very long alkyl chain and they also have a hydrophilic head group. So, what they do is that, if this is the water air interface; so, these molecules will actually interact with their hydrophilic head group, through the water and then their alkyl chain actually pops out from the water from the interface and then they just arrange themselves nicely in a parallel fashion.

So, you see there is a large drop and then after some threshold concentration, it is not changing much, because they have almost formed the kind of mono layer on the surface in the sense that, if you add more and more. So, then there is not much space that their highly crowded molecule and then if you still keep on increasing the surface, excess will not change much, because now the molecules will try to go inside more and more into the bulk phase, because there is no space available to go into the interface.

So, in this chapter what on in this section, what we just discussed is that, first we started with thermodynamics of interfaces and we talked about a model, which was developed by Willard Gibbs and we said that we can actually ignored the surface area or the not surface. So, at the volume by saying or by assuming that the thickness of the surface is vanishingly small, which you can take to be 0 and then we defined the surface tension and then we just try to write the first law, for the bulk phases as well as the interfaces and we give a concept of what is meant by the surface excess, which you define later mathematically and then we saw that we can actually divide this or these segregate.

This first law into different pieces one for alpha phase, one for beta phase, and one for the bulk phase and then we got equation like this and then we used some approach like the Gibbs Duhem equation. The similar approach which you use to derive the Gibbs Duhem equation and you have got this relationship. And we also made an additional constraint that we are considering the constant temperature to get an isotherm and then we found that we got a relation which is basically, a relationship between gamma and which is basically the capital gamma, the surface excess with small gamma, which is surface tension and how it is varying with the activity or the concentration and this is known as Gibbs adsorption isotherm and we saw that based on the Gibbs adsorption isotherm.

We can actually differentiate molecules into three different categories like; type 1, type 2, and type 3, and type 3 molecules are very interesting, which are known as surfactants, because they preferentially have a very high tendency or propensity to go into the interface than being stayed at the bulk surface, at the bulk phase. So, here always remember that we are plotting it as C 2 alpha meaning, we are actually increasing the concentration in the alpha phase, which means the concentration in the interface and the other phases will also increase and we are writing it as 2 1, in the sense that, it is basically chemical potential of the substance.

It is not actually component in the interface rather, we could instead of writing it as a component in the interface we could write it is a first component and the second component in the sense the first component here, is the say salt or the reverse micelle or the not reverse micelle sorry, the surfactant molecules and the first component here is just water. So, it is how much excess you are having of component 2, in presence of component 1 which is water. Water is always present.

So, 2 and 1 are here, for the components, it is not for the interface of the bulk interface and bulk. We are still preserving, this alpha and beta notations. So, we will be just closing this discussion here, and in the next lecture, we will be discussing about the kinetics of chemical reactions. So, we will be discussing how fast or how slow chemical reactions proceed and we will device models to explain those things.

Thank you.