Course: Adsorption Science and Technology: Fundamentals and Applications

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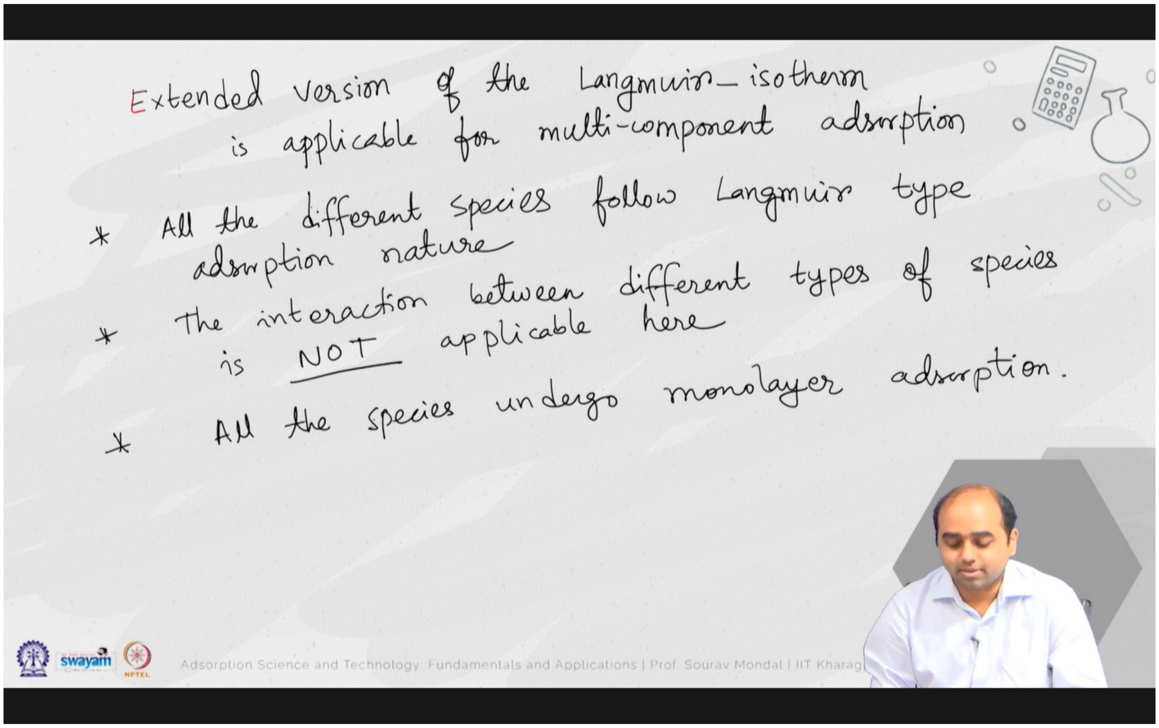
Week 02

Lecture 6 | Multicomponent Langmuir and Other Isotherms

Hello everyone, welcome to this lecture 6 on multicomponent adsorption. As you know often in adsorption there is a possibility of multiple you know species which is competing or which is actually adsorbed simultaneously during a process. So, in this case the adsorption is slightly competitive in nature as there is a possibility or competition between the molecules to actually you know compete for the same site. So, with this idea in mind the the classical single component Langmuir isotherm is actually extended to account for the multiple components or multiple species present in the system during a particular adsorption setup. it is often very relevant to quantify the selectivity of a particular species in a in the presence of a mixture. For example, in a wastewater treatment, let us say you will having a lot of different types of species which needs to be removed or separated from the system or from the mixture containing another you know a lot of other components.

For example, if you have a textile effluent which contains various types of dye you know other organic compounds then you have salts etcetera and specifically you want to separate one of the hazardous dye from there. So, it is important to quantify the selectivity or the separation factor of that particular targeted species among the other you know species which is present in that solution because most likely the the adsorbent that will be used for example, activated carbon is also quite sensitive or it is also can you know adsorb multiple components. So, selectivity of the target species in a mixture is very important and relevant. Same is true for let us say for CO 2 capture.

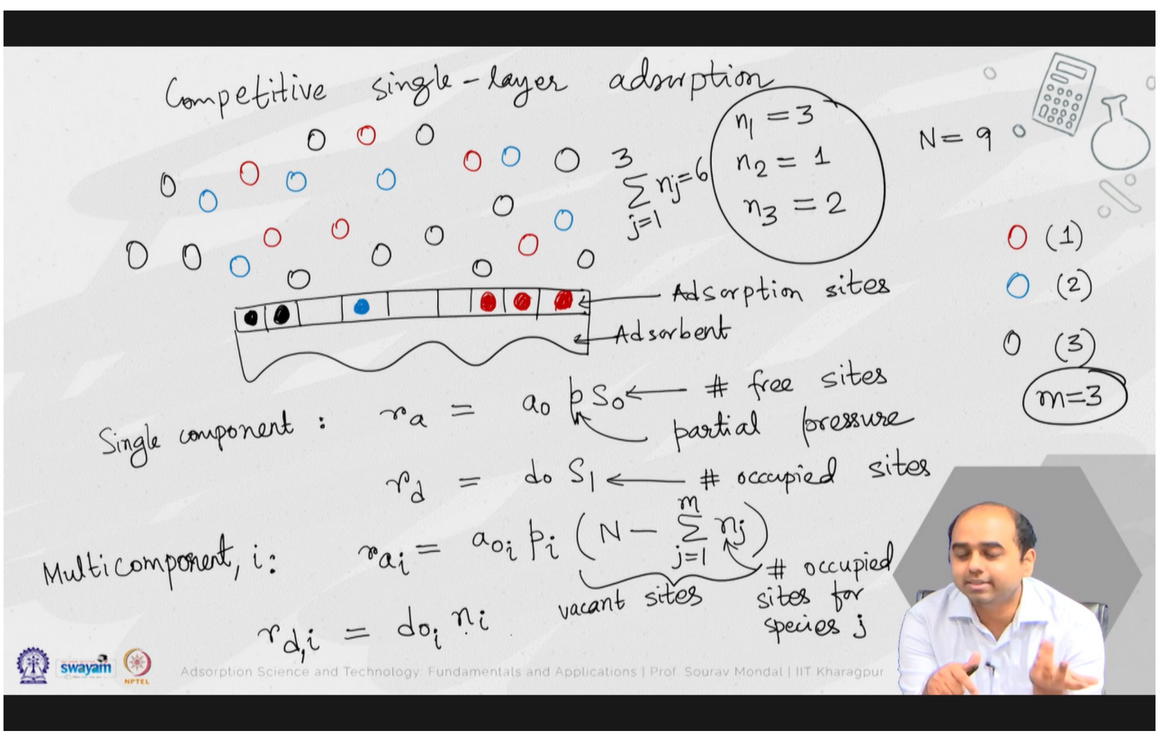


So, the the adsorbent which is used for you know particularly in the adsorbent based process of CO 2 capture and separation can also to some extent adsorb or separate nitrogen. So, it is very important to quantify or magnify the adsorbent capacities by engineering its molecular structure or its material properties. So, that the you know separation efficiency towards the desired or the particular component is more compared to the others. So, how does this relative separation efficiency or the selectivity is defined is also something that we will talk about and discuss in this lecture today. So, this extended version of the Langmuir isotherm is actually considered here. So the assumptions for this multicomponent adsorption stays the same as it is applicable for the Langmuir.

So it is assumed that all the species, all the different species follow Langmuir type nature the interaction between different types of species is absent which is also the case for single component. But there you had only one particular type of species now here in this case of different types of species there is also no interaction that is possible or that is considered interaction between between different types of species is not applicable here. And final one is all the species that we are considering they undergo monolayer adsorption. So, these are some of the you know important assumptions or considerations in this multicomponent adsorption problem which is basically an extended version of the single component adsorption. So, now let us see how does this derivative sorry this derivation goes.

It must be noted that even though there are multiple species it is still not possible that you know two different types of species can occupy one adsorbent site that is also strictly not possible in this case similar to I mean like the previous case where we had single component in that case it was strictly maintained that only one molecule will occupy only one adsorbent species so one adsorbent site Here also in the case of multiple you know species present the one adsorbent site can only be occupied by one species molecule of whatever type it is. So, the nature of adsorption is competitive in nature. So, we will try to understand how does this competitive single layer adsorption can be mathematically described. So, we take the same example we draw some you know sites for adsorption the number of adsorbent sites which is available is constant. So, these are the adsorption sites and let us say we have different types of species molecules which are present.

So, it is like a mixture. and all of them has equal probability of getting attached or getting adsorbed. So all of these types can be adsorbed either in any one of these adsorption sites and all the adsorption sites has equal probability of binding to any of these species. So, the sites are not species specific they allow adsorption to any type of species and that is what all the molecules you know compete for the same site is is possible. So, the total number of sites is possible is constant and each molecule can occupy only one particular site.



So, for the single component for single component if you recall this rate of single component this rate of adsorption is proportional to the number of free sites to the partial pressure of that component and it is multiplied with the adsorption rate. So this is the number of free sites, this is the partial pressure. and this is the adsorption constant. Similarly, for the rate of desorption it is the desorption constant multiplied with the number of occupied site. The same idea is used in the multi component system as follows.

So, in the case of the multi-component system, the rate of adsorption is particularly defined for each you know species. So, the rate of adsorption for let us say for any ith species because now it is species specific. So, I will write this as Rai. a 0 i then partial pressure of that species and the available free sites. in the system.

Now the available free sites can be understood as like the subtraction of the occupied sites with rest from the total number of sites. So I can write this as this is the total number of sites minus the summation of all the occupied sites by the other species. So, where j corresponds to the number of species 1 to m. So, nj is the number of occupied sites species j for a particular species j where j can vary from 1 to n depending on the number of components that you have. So, let us say in this case m is equal to 3 there are 3 types of species molecules which is represented by 3 different colors.

So, this is what is representing that j is equal to m is equal to 3. So, all the 3 types of species and so n. Let us say I define the red colour as red colour then the blue colour then the black colour. 1, this is considered as 2, this is considered as 3. So, N 1 which is the number of occupied sites for red species is equal to 3, N 2 is for the blue species which is 1 and N 3 is the black species which is equal to 2 in this case. So, the total number of species in this roughly the schematic here is capital N which is equal to 9 right.

So, the number of available sites as you can understand is 9 minus 6. So, 3 and this 6 are the total number of occupied sites is nothing, but the summation of N j where j is equal to 1 2 3. So, in this case the m or the number of species is equal to 3 and on summing them up you can find out the number of occupied site and if we subtract that the number of occupied sites from the total number of sites which is available one can get the number of vacant sites. So, effectively this represents the total number of vacant sites. which is available for adsorption of any particular species.

So, now, within this three vacant sites it the the blue or the red the black any species represented by I can occupy any of this vacant sites which is possible. So, all the you know species have equal chance or probability of occupying any of these vacant seeds which is unoccupied yet and that is why it is proportional. So, the number of vacant sites which is available directly affects the rate of adsorption directly affects the adsorption rate for any species which is represented by i. in the case of desorption rate for the I8 species it is the constant and multiplied with the occupied site by that particular species. So, in this case please note that I have written down as n i because this is we are writing for the ith species whereas, when we are summing it up I wrote a different index j, but so as not to confuse our self that j is not equal to i.

I mean j could be equal to i, but j j we have written as separate summation index. So, as to consider that j varies from 1 to all the species. And for any ith species this is what you get the number of vacant sites is coming out from the you know number of occupied sites by all the species. In the case of the desorption rate it is n i or small n i because the number the number of occupied site by that particular species will affect the rate of desorption for that species. That is what we wrote here and we tried to emphasize that the number of occupied sites by a particular species will affect its desorption rate.

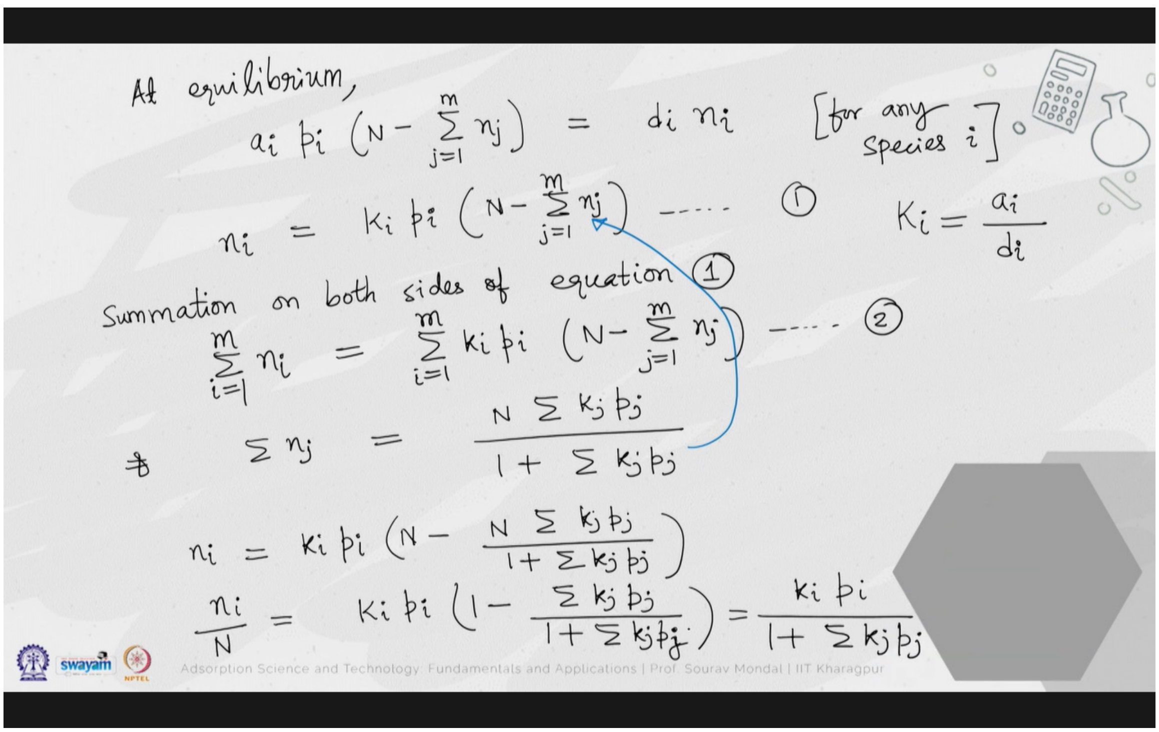
So, the number of occupied sites by the black molecule will not affect the desorption rate of you know this red molecule, but this is not the case in the in the situation of adsorption. So, the total vacant sites which is of course, the subtraction of the occupied sites from total number of sites which suggest that let us say for adsorption of the blue species or the adsorption of the red species whatever the available sites which is present after getting occupied by any species is is available. So, which means the occupied site by the black molecule will play a role in studying the rate of adsorption or in predicting the rate of adsorption for red species because the red species will can only occupy the vacant seeds and the vacant seeds are you know available based on the level of adsorption or occupancy by the other species. So, that is how the you know effect of the other species comes in whereas, in the desorption case where where whatever be the number of you know occupied sites by blue or red it is not affecting the desorption rate of the red species, but for the case of adsorption this is not true and there is a effect. of the occupancy of the other molecules for during the adsorption for another molecule.

So, if the for example, if the blue molecules wants to get adsorbed the occupancy level by the black and the red molecules will also play a role because they consume part of the available sites open to this blue molecule. Now, let us try to equate these two because you know at equilibrium these two are equal. So, at equilibrium these two rates in this case will be equal. So, which means the rate of adsorption for any species i will be equal. So, this is for any species or any species or component. So, now let us try to do some algebraic manipulations of this equation.

Let us also define the equilibrium constant for this particular species as ki which is the ratio of the adsorption rate to the desorption rate. So, in this case we can define small ni as equal to ki pi. Now on the left hand side and on the right hand side in both cases we have this small nj and on the right hand side we have this within the summation term. So let us call this as equation 1. Now let us try to do a summation on both sides of equation

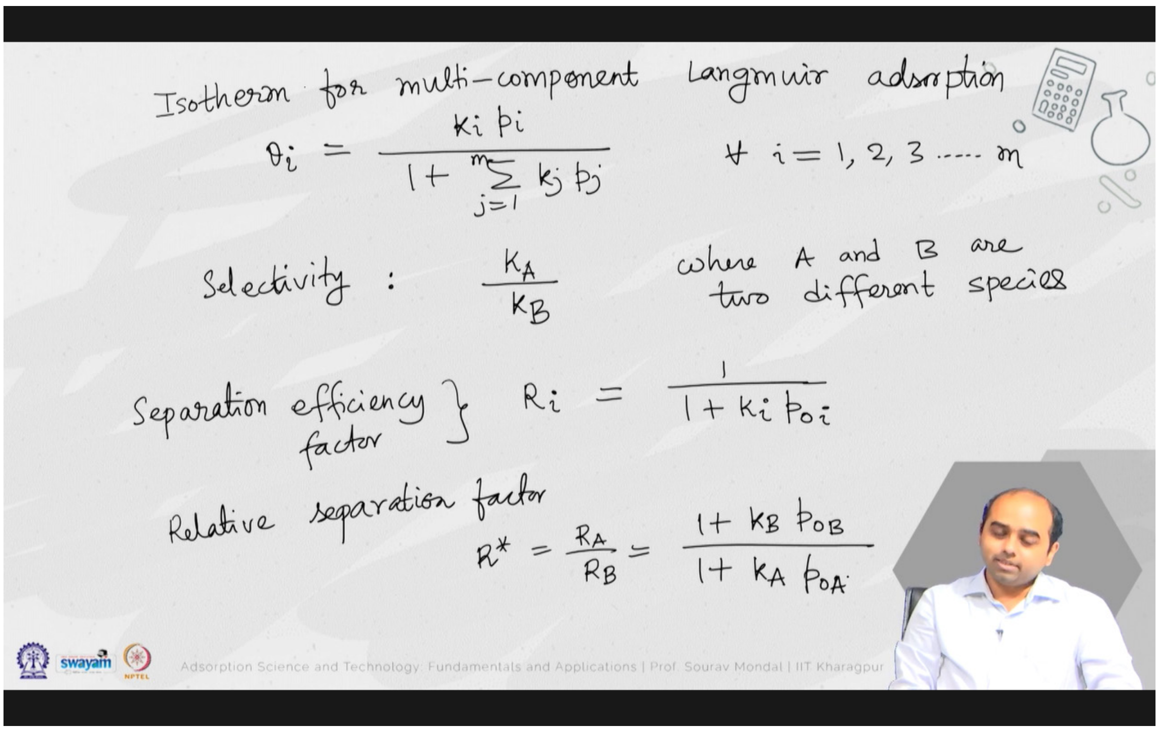
1. So it suggests so if I do this summation whatever be the index whether it is i or j I have to sum it up over m number of components. So, whether it is i or whether it is j this can be essentially you know summed up within this total number of components that we have. Now, if we try to rearrange this expression we see that summation this equation this expression that we call it at as number 2 this can be again rearranged with you with I mean just on the left hand side and the right hand side in both cases you have. this summation n j.

So, this summation of n. So, please note that summation of n i or summation of n j both are actually same because both varies from i from 1 to m. So, let us write both as you know n j and remove this confusion in this case. So, this will be equal to in right I mean i and j in this are now makes same sense. So, that is why I take this leverage write down in terms of this N j. And please note that this summation of N j can be represented in terms of the summation in terms of this form where capital N is actually the total number of sites that is present in the system.



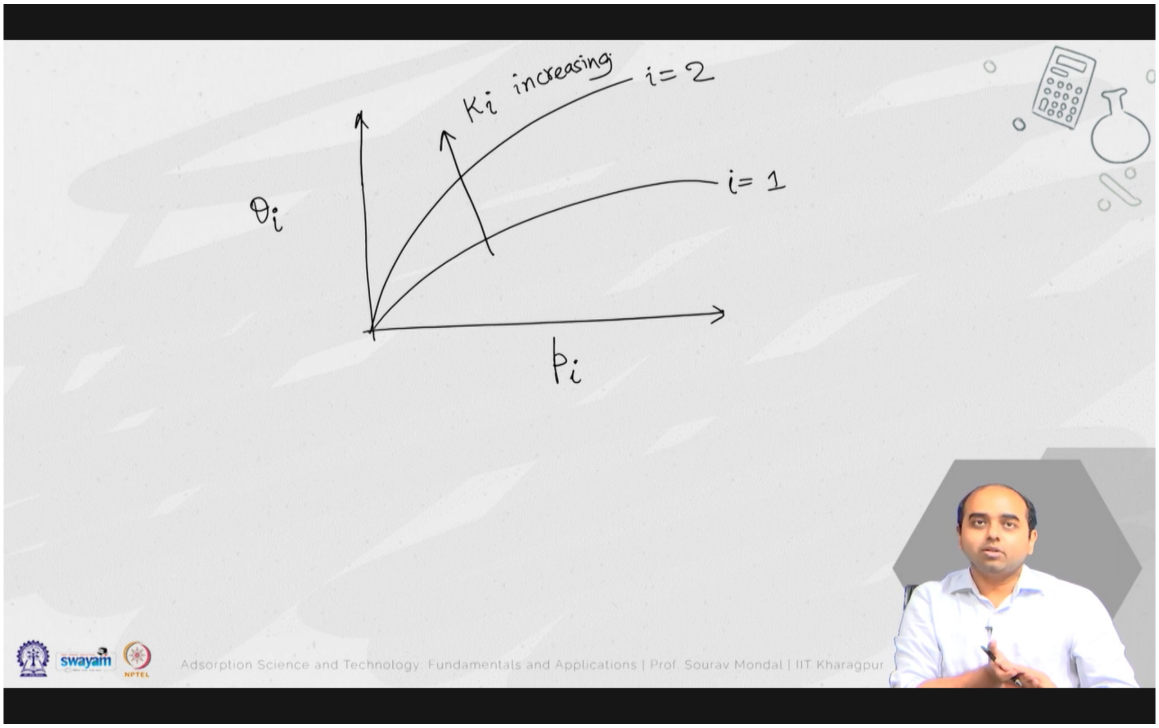
Now, this equation this version that we get here can be you know transferred back to this point here. So, on doing so we get so I am just writing the mathematical steps on this insertion here this is possible. Now, I can divide n i by capital N as k i p i 1 minus as this form. Now this is nothing but equal to k i p i by summation of 1 plus this one and we all know that n i by capital N is nothing, but the partial coverage for that particular species i . So, in a in a summarized form the isotherm equation for this multi component system isotherm for multi component Langmuir adsorption is theta i is equal to k i p i divided by 1 plus the summation of all the other components j is equal to 1 to m.

Now, in this case it may be understood that the denominator of this expression represents the the relative effect of the adsorption of the other species because this equilibrium constant K j is different for different species. So, adsorption of the ith species is getting affected by the other species through this denominator summation term. So, in other in in this case the definition of the selectivity becomes very important and we must you know emphasize that the selectivity in this case which is applicable here is defined as like K a by K e p. So, for a preferential. So, where A and B are two different species.



So, like this it can be defined for any species present in the mixture and this selectivity should be larger than one much much larger than one. So, that preferentially one of the particular species is adsorbed more compared to the other this other species. In the case of selectivity or the separation efficiency in this case separation efficiency So this separation efficiency or the separation factor that we have defined for this for the single component can also be defined here would be like 1 plus K i P 0 i. So the selectivity in that respect or the separation relative separation efficiency relative separation factor this r star which is r a by r b can be defined as 1 plus k b P O B plus 1 plus K A P O A. So, this is how typically you know this Langmuir isotherm separation efficiency can be discussed. In terms of you know different this its its profile with respect to the partial pressure it follows Langmuir type nature for this partial for any particular species i. So, this is for you know ith species let us say i is equal to 1 it could be other one i is equal to

2. So, depending on the value of the you know ki the Langmuir isotherm or this separation efficiency can be more or less and accordingly the isotherm nature of the isotherm can be different. So, at particular low partial pressures a particular species may still be adsorbing whether the other one has reached already its equilibrium concentration that that kind of scenario is highly possible in this.



So, with this I close this lecture in the next one we will talk about the other types of adsorption isotherms which is very popular and relevant and I hope all of you found this useful and you like this lecture. Thank you.