Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 01

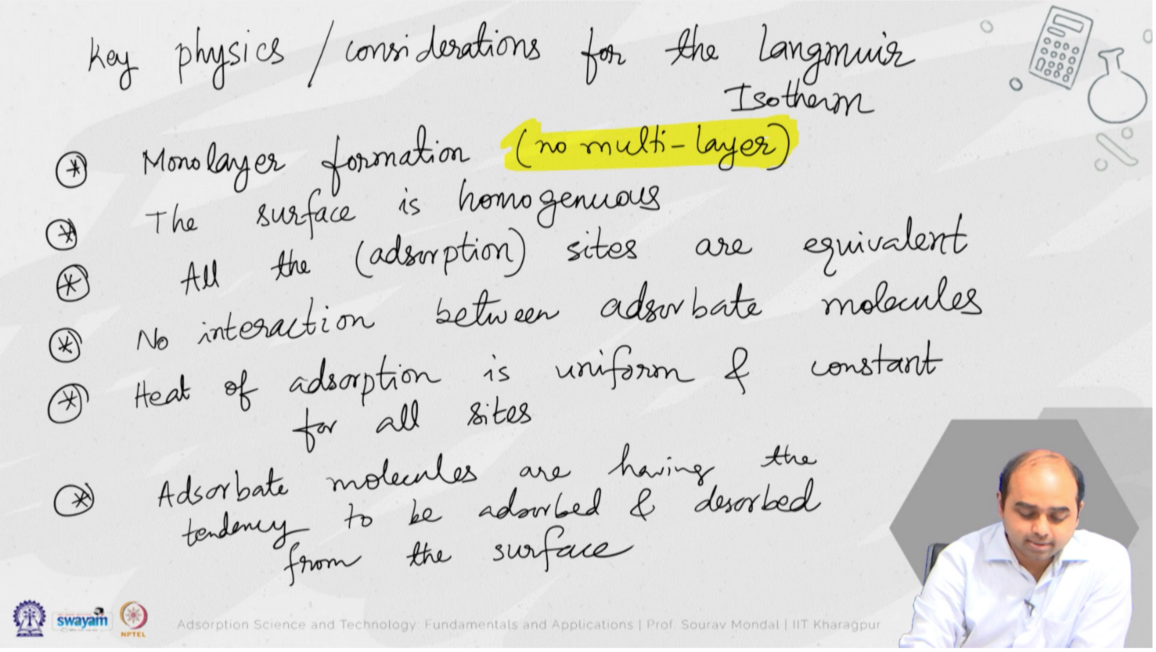
Lecture 5 | Langmuir Isotherm

Hello everyone, welcome to this course on adsorption science and technology. Today we are going to talk about this Langmuir isotherm, its details, its derivation, its key features and assumptions, limitations. So, let us look into what we mean by this Langmuir isotherm. Essentially, Langmuir isotherm is a adsorption isotherm model which helps us to explain the monolayer formation. So, the key physics which is present behind this Langmuir isotherm are as follows. So, you can also consider them to be the assumptions behind this model key physics or considerations for the Langmuir isotherm model.

The first important assumption or consideration is monolayer formation. So, by monolayer formation, we mean that the layer of the molecules deposited or bound to the adsorption is a single molecule thick. So, there is no multiple layers which is forming and it is only a single molecular layer thickness of the molecules or the adsorbate species which is attached to the adsorbent. Another important is that the surface of adsorption is homogeneous.

All the sites or all the potential you know adsorption sites are equivalent. So, this essentially means that there is equal probability of adsorption or attachment of a particular species in any of the available adsorption species, any of the adsorbent you know sites. Next important is this no interaction between the adsorbate molecules after it is adsorbed. So, no intermolecular interactions or inter particle interactions that is possible or considered in this model. The heat of adsorption is uniform and constant for all the sites.

So, this again is a sort of an elaboration of the third point where we said that all the adsorbent sites are equivalent. This essentially emphasizes that the heat of adsorption or the thermodynamics of the adsorption process for all the sites or any site available is same and there is no absolutely no distinction between the sites and there is no preferential attachment to any particular region or any particular site. Another important thing is that this adsorbate molecules are having the tendency to be adsorbed and desorbed from the surface. So, this essentially rules out that there is no possibility of further chemical reaction or further attachment of these species into the matrix or into some other sites. So, site-site interaction is absolutely ruled out and it is assumed that the molecules which are attached they have a tendency to be only you know only absorbed and dissolved from the surface.



Key physics / considerations for the Langmuir Isotherm

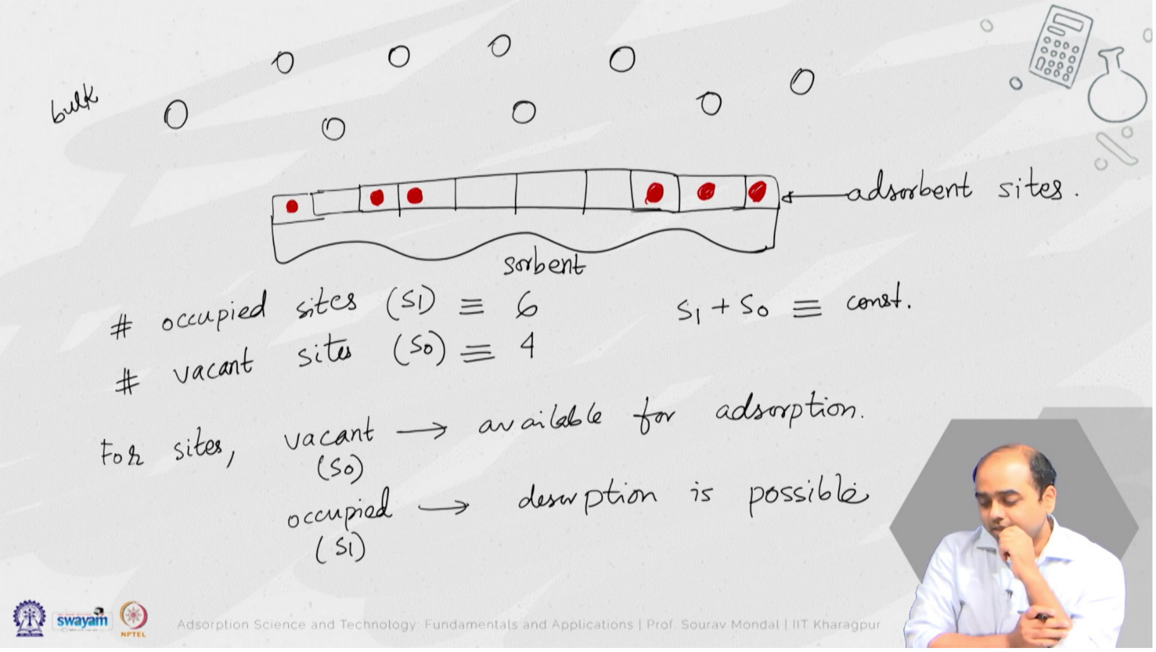
- (*) Monolayer formation (no multi-layer)
- (*) The surface is homogenuous
- (*) All the (adsorption) sites are equivalent
- (*) No interaction between adsorbate molecules
- (*) Heat of adsorption is uniform & constant for all sites
- (*) Adsorbate molecules are having the tendency to be adsorbed & desorbed from the surface

So, these are the key physics or the considerations behind you know the Langmuir isotherm and some of them are some of them are quite obvious and it is also applicable for other types of ah adsorption isotherms, but at least in this case for the Langmuir model these are the different physics that is typically considered and is assumed to be you know happening during the process of adsorption. Now this one more thing I must mention here that there is no multilayer formation that is allowed or you know possible and this is something I am you know highlighting this point or the first point when I said that it is only strictly monolayer. And, just to emphasize that there is no multilayer which is possible or which is happening in this case. Now, let us see that how this you know this equation or the mathematical model, which describes the Langmuir isotherm is actually derived or is actually conceived Let us consider a site where there is some available space for different molecules to be attached. We define some molecule species for this moment and in this class we are talking about a single component adsorption.

In the next class we will talk about multi component Langmuir isotherm or multi component adsorption where we will consider different types of species. But in this we are considering only you know single component. So, it is only one particular type of species, and we are considering some adsorbent sites. So let us say we have some adsorption sites like this and in this adsorption sites these are the bulk gas or the bulk molecules and this is let us say the adsorbent sites. So this is essentially our adsorbent.

There is equal probability of any molecule attaching to any of these at ah adsorption sites also it must be noted that only one molecule can get attached to only one particular site. So, there is not it is not possible that there could be multiple you know molecules or getting bound or getting adsorbed at the same adsorption site. So, one molecule in one adsorption site. So, let us consider few adsorption you know molecules which are already adsorbed. So, there are some vacant sites and some you know occupied sites.

So, the occupied let us call the number of occupied sites here. S1 in this case as 6 number of vacant site let us call that as S0 as 4. So, total number of sites like this vacant plus the adsorbed site is always constant So, that is from the conservation of the total available total number of adsorbent sites they are neither created nor they are destroyed. So, when desorption happens when adsorption happens total number of adsorbent sites remain fixed it is only that different locations which is occupied or which is vacant gets changed during the process. Now, let us see that for sites which are vacant they are available for adsorption right.



occupied sites $(S_1) \equiv 6$ $S_1 + S_0 \equiv$ const.

vacant sites $(S_0) \equiv 4$

For sites, vacant (S_0) → available for adsorption.

occupied (S_1) → desorption is possible

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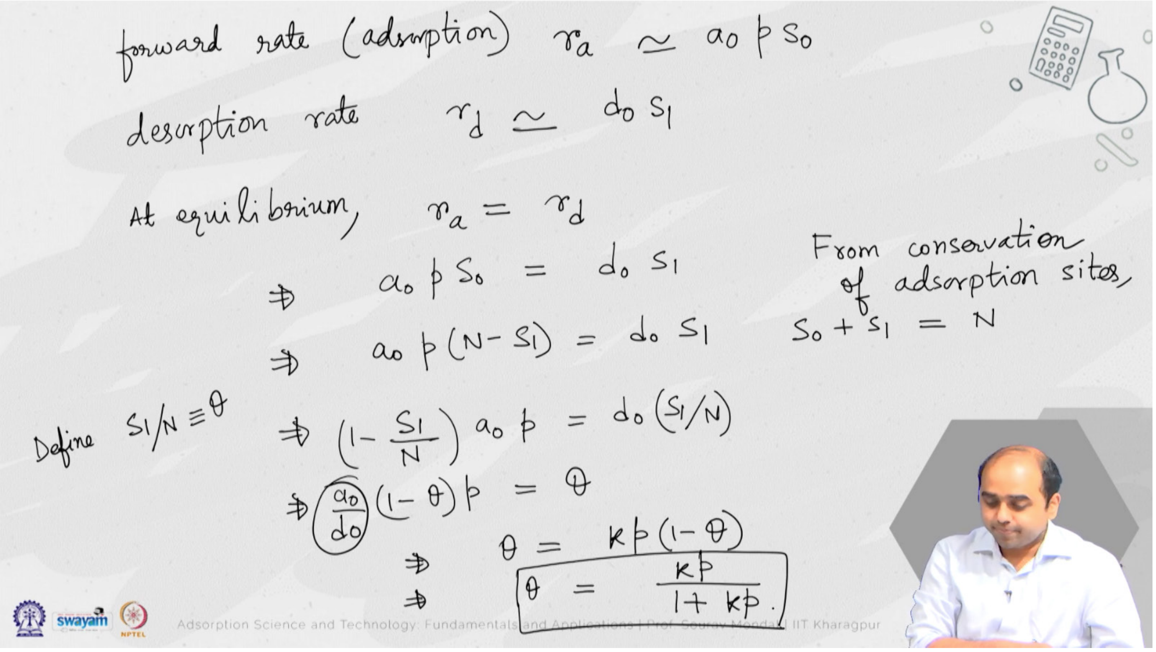
So, the S0 sites are available for adsorption and the sites which are occupied from them only desorption is possible. So, when the system is in equilibrium the rates of this adsorption and the rates of the desorption is equal. So, let us try to understand what would be the adsorption rate or the forward process rate. So, the forward rate which is the adsorption case. So, this would be proportional. So, this would be proportional to the number of available vacant sites which is S0 as well as the partial pressure of the gas in the bulk phase. Higher is the partial pressure higher would be their you know tendency or their kind this energy that can lead to this adsorption right.

So, partial pressure is equivalent to the concentration. So, the chemical potential in the bulk phase would be higher and naturally this will lead to this adsorption towards a lower ah energy state or towards a lower minimizing the chemical potential it can move from high entropy to a low entropy state. So, pressure actually determines that factor and to make this a constant we will have a adsorption rate. backward or the desorption rate. So, desorption rate, would be proportional to the number of occupied sites S1 right only this.

So, there is no, you know, this pressure etcetera which is you know which makes sense in the case of desorption. So, this would be multiplied to the you know some constant which takes into account of the you know conversion of the number of sites to the rate. So, that is like the dimensional constants. So, for at equilibrium since this is a spontaneous process the rate of adsorption would be equal to the rate of desorption. So, mathematically this means that I can equate the two rates now from mass from conservation of this you know adsorption sites S0 plus 1 is constant let us call that n total number of sites.

So, this can be written down as right. So, we can define S1 by n as the fraction of the sites which is covered. Let us call that as something like theta. So if you rearrange this equation we can say that. So, this factor the ratio of the forward rate to the backward rate can be represented by an equilibrium constant very similar to this reversible equilibrium chemical equilibrium that you are already aware of where the rate of the forward reaction divided at the ratio of these two is represented by an equilibrium constant.



forward rate (adsorption) $r_a \simeq a_0 p S_0$

desorption rate $r_d \simeq d_0 S_1$

At equilibrium, $r_a = r_d$

$$\Rightarrow a_0 p S_0 = d_0 S_1$$

From conservation of adsorption sites, $S_0 + S_1 = N$

$$\Rightarrow a_0 p (N - S_1) = d_0 S_1$$

Define $S_1/N \equiv \theta$

$$\Rightarrow \left(1 - \frac{S_1}{N}\right) a_0 p = d_0 (S_1/N)$$

$$\Rightarrow \frac{a_0}{d_0}(1-\theta) p = \theta$$

$$\Rightarrow \theta = kp(1-\theta)$$

$$\Rightarrow \boxed{\theta = \frac{kp}{1+kp}.}$$

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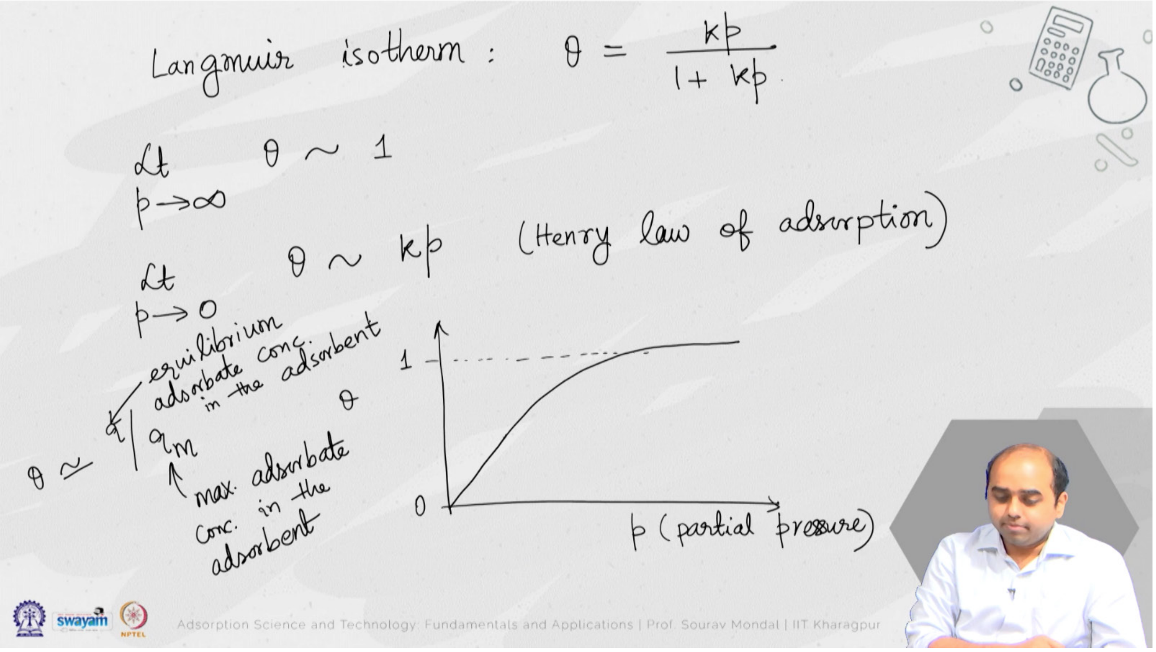
So, this can be treated as a constant. So, we can write like this or in other words this represents. So this is the algebraic step and this you know confirms the this mathematical model which represents the fraction of the sides which are covered with respect to the partial pressures. Now in the limiting condition in the in the two limiting conditions so the Langmuir isotherm equation is this. Now, in the limit of when p is very high, when the limit of p is very high, this theta is proportional to 1.

So, which suggest that most of the you know sites which are available for adsorption would be covered or in other words the adsorption would be close or would be equal to almost the maximum adsorption capacity or the maximum adsorption rate or the maximum capacity that is available for all the adsorbents right. Similarly, when this p is small, this theta takes this form. So, this is more of the Henry's law of adsorption which is a linear law which suggests that the you know the amount of the coverage by these molecules or by this adsorption is proportional to the partial pressure of the gaseous system. So, these are the two limiting regimes of this scenario. So, if one tries to plot this theta versus p this would look like a linear regime and then it switches to a constant value and this constant value approaches unity.



Langmuir isotherm : $\theta = \frac{kp}{1+kp}$

$\underset{p \to \infty}{Lt} \quad \theta \sim 1$

$\underset{p \to 0}{Lt} \quad \theta \sim kp$ (Henry law of adsorption)

$\theta \simeq q/q_m$

equilibrium adsorbate conc. in the adsorbent

max. adsorbate conc. in the adsorbent

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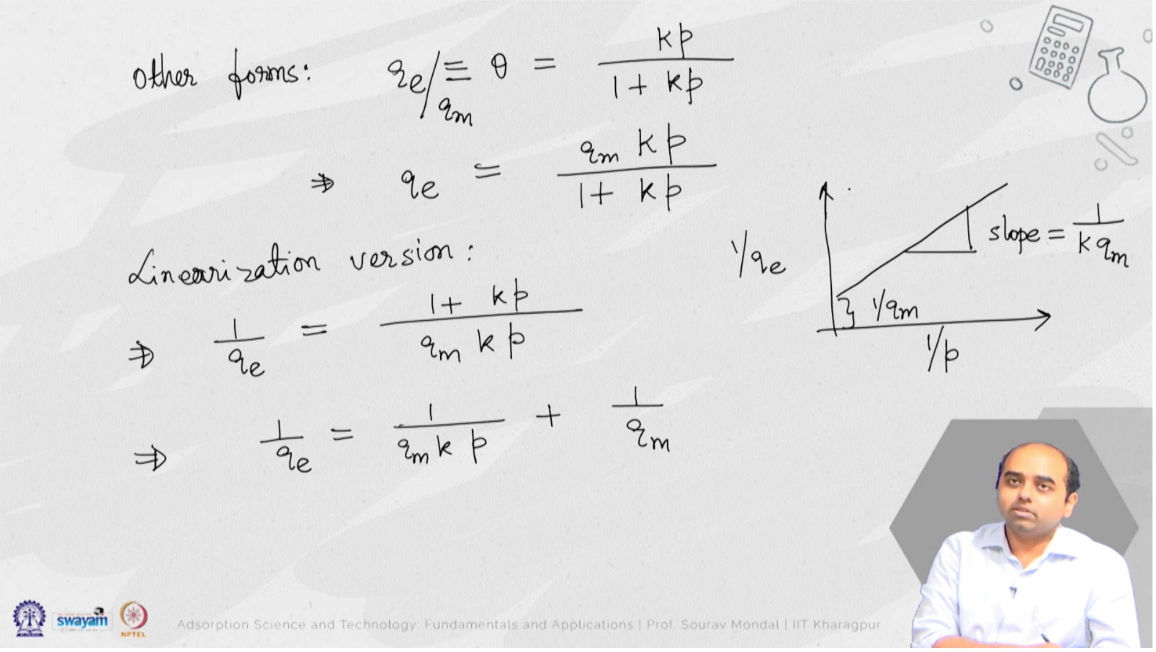
So, this would be the you know the typical profile, of this Langmuir isotherm. Let us try to understand what this theta represents in more physical ah terms. So, typically this theta even though the way we have derived it represents something related to this ratio of the surface coverage. In other words this can also represent the fraction of the molecules or the you know this fractional concentration of the molecules with respect to the total concentration or the maximum possible adsorbate concentration, within the adsorbent phase. So, theta can also be used to represent something like Q by Qm where Q represents the concentration of the adsorbate species in per unit mass of the I mean concentration itself means unit mass per in the adsorbent and Qm represents the maximum adsorbate concentration that is possible in the adsorbent and Q represents the equilibrium adsorbate concentration in the adsorbent.

So, this is how typically the Q can be represented and this K represents the factor or the equilibrium constants. So, there is also other forms of this Langmuir isotherm. So, in terms of Q, so Qe by Qm which essentially represents your theta can also be used to represent the same Langmuir isotherm or in other words Qe can also be used to write something like this. There is a linearization possible a linearized version which is possible. So, if you try to take the inverse on both sides this will be rearranged in this form .

So, with a plot of 1 by Qe versus 1 by p you will expect a linear plot of the same non-linear equation where the intercept is 1 by Q m and the slope is 1 by k Qm. So, typically you know the experimental data where you typically obtain the equilibrium concentration with respect to the partial pressure they are sometimes instead of a non-linear regression to evaluate these constants Qm and k, only the linearized version is also you know plotted and then from the linear regression you can work out what would be the value of these regression coefficients or these constants.



Other forms: $q_e/q_m \equiv \theta = \frac{kp}{1+kp}$

$\Rightarrow q_e = \frac{q_m k p}{1+kp}$

Linearization version:

$\Rightarrow \frac{1}{q_e} = \frac{1+kp}{q_m k p}$

$\Rightarrow \frac{1}{q_e} = \frac{1}{q_m k p} + \frac{1}{q_m}$

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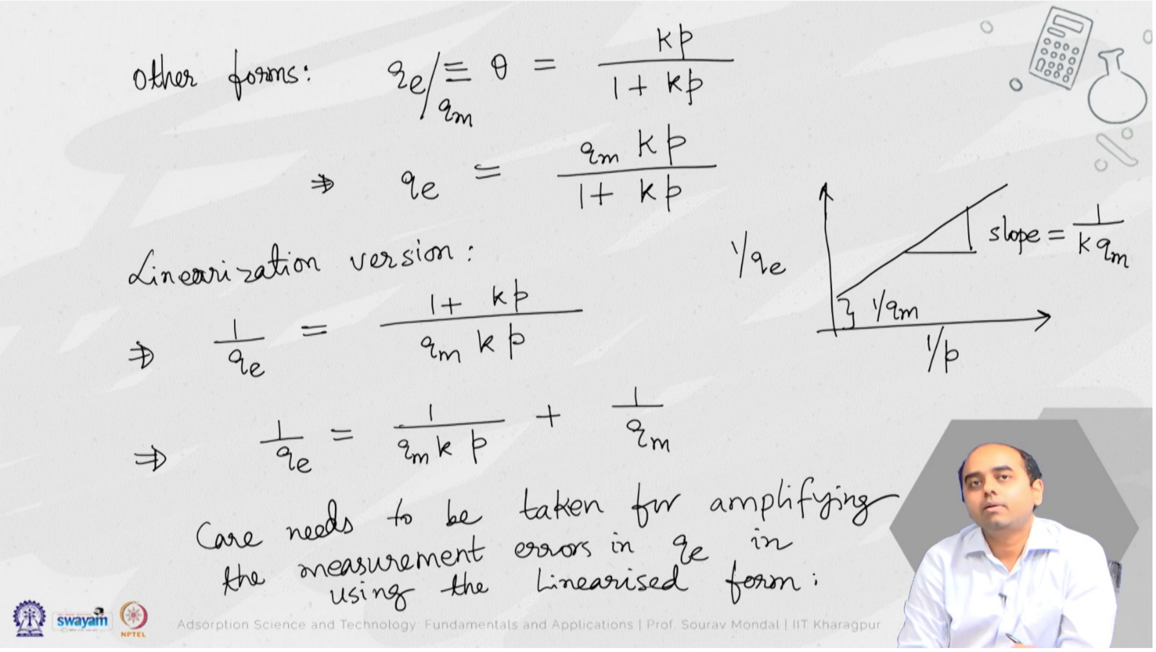
But please be aware that there is a high probability or there is a high uncertainty in magnifying or amplifying the errors encountered during the experiments because when you are taking the reciprocal of the value of this Qe. The errors that are associated during the measurement of this Qe will get magnified at particularly at low values of Qe. So, this is something that needs to be aware of and one should be careful in you know, trying to relate or trying to work or calculate the coefficients or the regression coefficients from the linearized version of this model.



Other forms: $q_e / q_m \equiv \theta = \frac{kp}{1+kp}$

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Linearization version:

$\Rightarrow \frac{1}{q_e} = \frac{1+kp}{q_m k p}$

$\Rightarrow \frac{1}{q_e} = \frac{1}{q_m k p} + \frac{1}{q_m}$

Care needs to be taken for amplifying the measurement errors in q_e in using the Linearised form:

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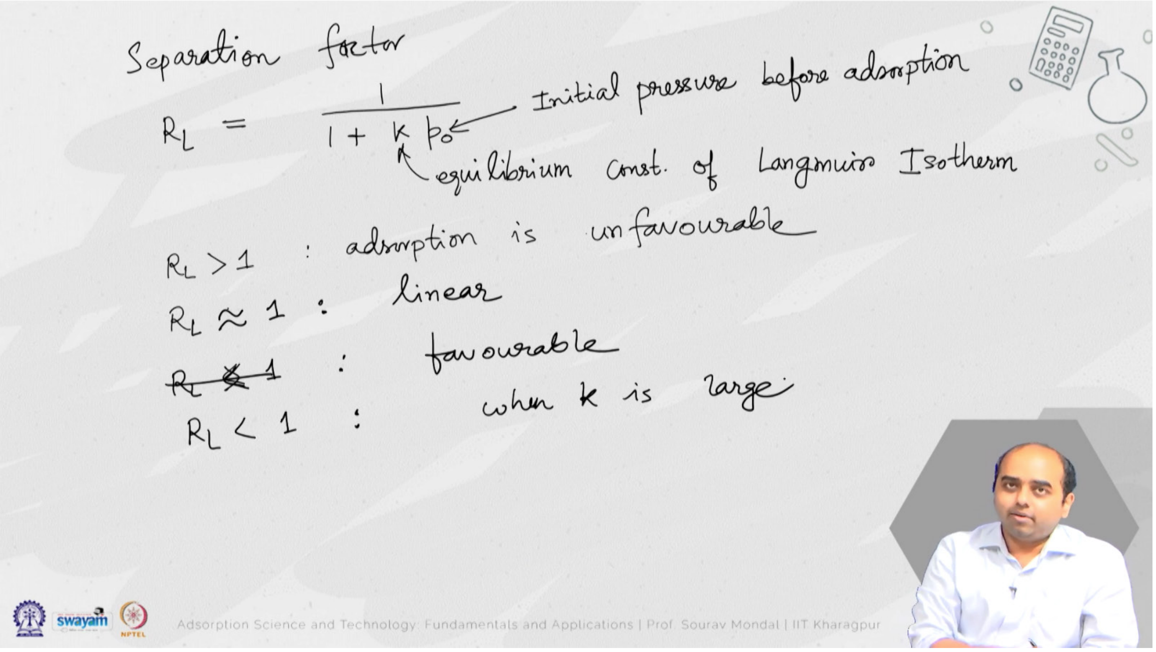
I want to talk about the separation factor in this case which is often referred to by many researchers working in this area. So, the separation factor RL is denoted by this form which is dependent on the you know this equilibrium constants of the Langmuir isotherm. And this P0 represents the initial pressure before adsorption. So, one would get a idea about the level of separation during this process of adsorption. So, typically there are 3 regimes or 3 different possibilities.

So, if RL greater than wall, so which suggest that adsorption is unfavourable. It clearly understood that RL can be greater than 1 possibly when k, the estimation of k is negative. We suggest the process is not driven by adsorption or separation is not driven by adsorption, when RL is close to 1 this is linear the process is linear and when particularly RL is greater than 1 this is favorable. So, it is highly desirable that the separation factor is much much larger than 1 to a sorry when separation is less than 1, adsorption is highly favorable and this ensures that this is possible when K is large. So, these are the you know these different possible regimes and one can quantify the level of separation that is possible in this adsorption process using the Langmuir isotherm.



Separation factor

$$R_L = \frac{1}{1 + k\,p_0}$$

← Initial pressure before adsorption

equilibrium const. of Langmuir Isotherm

$R_L > 1$: adsorption is unfavourable

$R_L \approx 1$: linear

~~$R_L \ll 1$~~ : favourable

$R_L < 1$: when k is large

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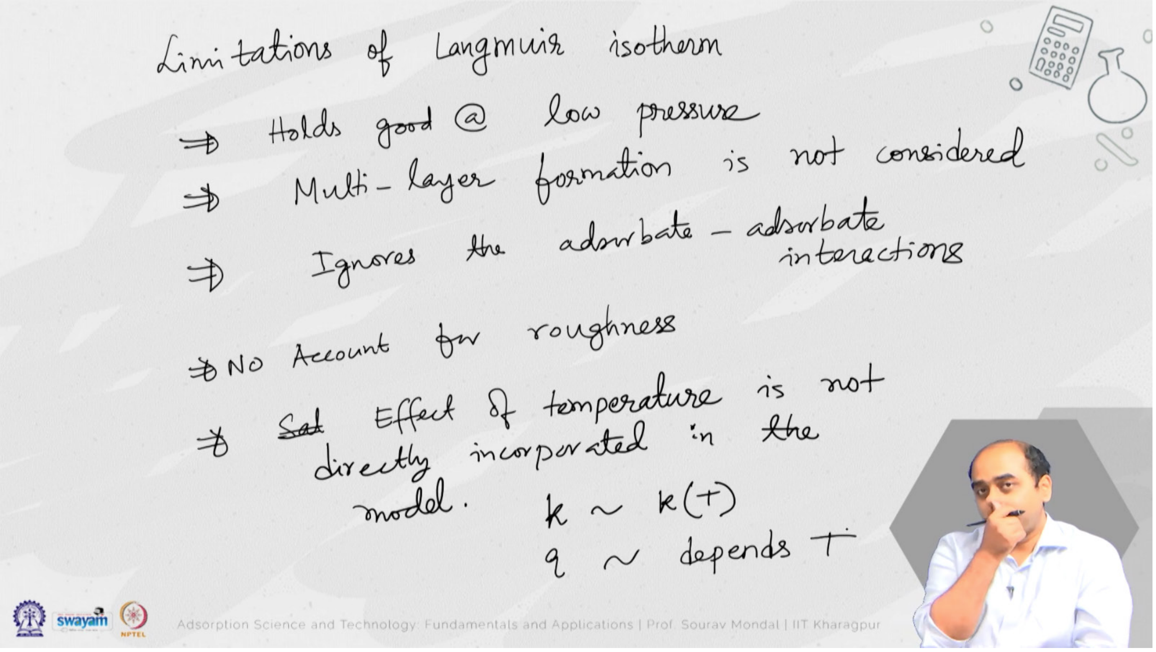
Before we end today's class I will quickly talk about or just you know mention the limitations of this Langmuir isotherm as this is very important to also understand that. So, this Langmuir isotherm is good or holds good at low pressure. This is particularly the reason that there is no multilayer formation. So, at high pressures this is of course, not good. Multilayer formation is not considered which could be a possibility in most cases when you operate at high pressures.



Limitations of Langmuir isotherm

⇒ Holds good @ low pressure

⇒ Multi-layer formation is not considered

⇒ Ignores the adsorbate – adsorbate interactions

⇒ No Account for roughness

⇒ ~~Sat~~ Effect of temperature is not directly incorporated in the model.

$k \sim k(T)$

$q \sim$ depends T

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It ignores the adsorbate adsorbate interactions. There is no account for roughness of the surface. So, essentially this means it is you know uniform or it is homogeneous which is of course, one of the assumptions and this the effect of temperature is not directly incorporated and in the model. Of course, this is not a big limitation the last point because generally what is done is that at different temperatures you try to get the Langmuir isotherm model and generally the k the constant and the equilibrium constant is a function of the temperature. But, nevertheless the Qm or the saturation value also sometimes you know depends on the temperature which is which is not at all accounted for in this model.

So, with this I will close this lecture see you all in the next lecture hope you find this useful. Thank you.