Course: Adsorption Science and Technology: Fundamentals and Applications

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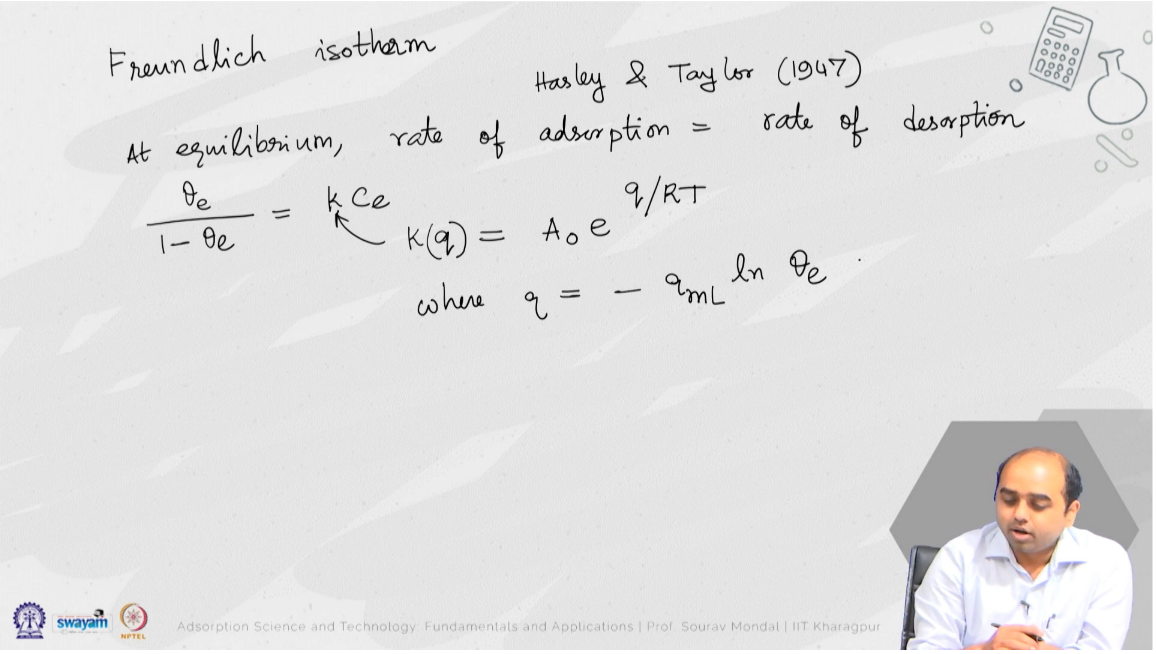
Week 02

Lecture 7 | Other Important Isotherms-Continued

Hello everyone, welcome to this class on this important isotherm. So, in the last lecture you have noticed that we focus or we concentrated on the multi component Langmuir isotherm which is an extended version of the single component theory. But, many a times the Langmuir isotherm is not so important and it is necessary to consider other types of adsorption models. And over the last 70, 80 in fact, some of these isotherms dates back to 1920 and 1930s. So, almost for over a century there have been various works done on different kinds of adsorption isotherms. We will try to discuss some of them in this lecture itself and see what are the you know major considerations behind the application of that particular isotherm and when it is applicable what is the you know physics behind it and so forth.

So, if the first major popular isotherm is the Freundlich isotherm. So, in this case of the Freundlich isotherm, it is basically a pseudo I would say a pseudo empirical model because it has some basis or some connection with the Langmuir type model. So, it is not entirely empirical in nature. But of course, this is derived or this is emphasized from a different you know empirical observations which actually helps in correlating or describing some of the you know adsorption behaviors which is not explained by the monolayer adsorption or the Langmuir isotherm.

So, this is represented as a sort of sometimes it is represented as a sort of the multilayer version for adsorption on heterogeneous surfaces too. So, let us look into that how this line this Freundlich, which isotherm is evolved. So, the Freundlich isotherm is a non-linear equation or non-linear adsorption model. Of course, it can be linearized and there are also use of the linearized version. But first let us try to understand this how this was originally evolved.



Freundlich isotherm

Hasley & Taylor (1947)

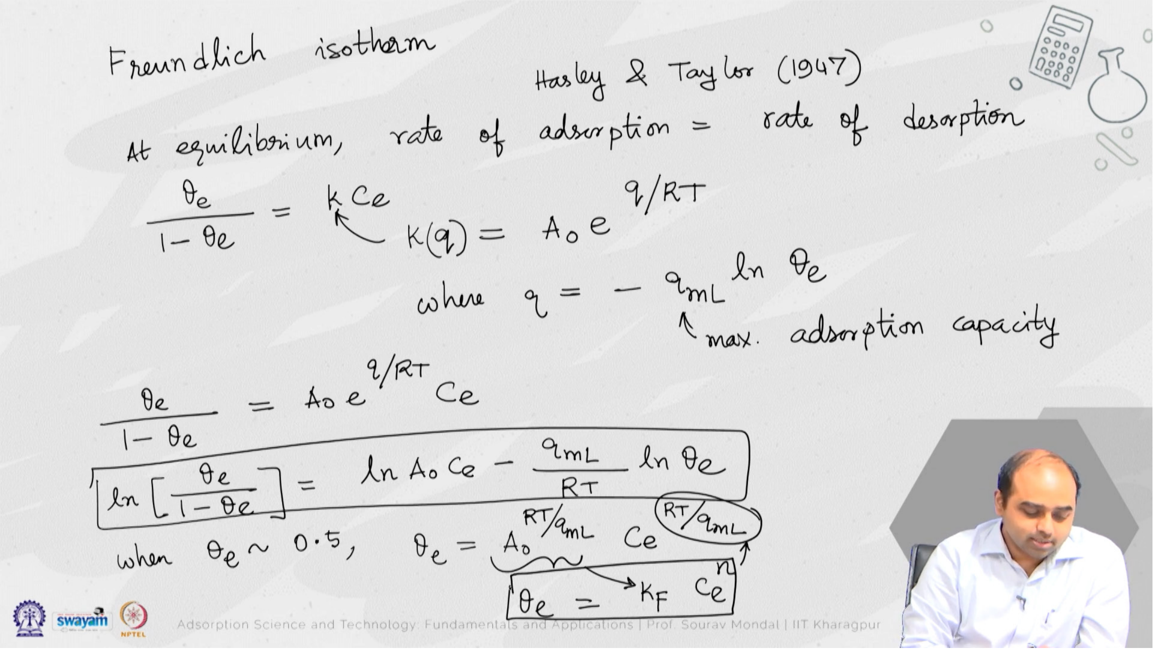
At equilibrium, rate of adsorption = rate of desorption

$$\frac{\theta_e}{1-\theta_e} = k C_e \qquad K(q) = A_0 e^{q/RT}$$

$$\text{where } q = - q_{mL} \ln \theta_e .$$

So, classically back in you know this 1947 and these two people Hesley and Taylor were. If you look into the research reference from 1947 from these two people, they have derived this Freundlich isotherm model with some improvisations from the Langmuir isotherm. So, at equilibrium we know the rate of adsorption and desorption are same. So which means that this theta at equilibrium let us represent that as theta e. In the previous class this is what we have seen as to be the theta. Instead of partial pressure I am writing this in terms of the equilibrium concentration which is also possible particularly for liquid systems.

So for liquid systems we talk about the concentration, for gaseous system we talk about the partial pressure. So this is all at the equilibrium. Now, this instead of this k, there is this work by Hesley and Taylor, they have proposed that this k is essentially a function of this q as something like this. So, where this q is represented in this form. So, of course, in this case as we are talking about q in terms of the equilibrium this would be related to the equilibrium theta e value and this q is nothing, but the equilibrium value of this theta e because the k that we are evaluating is at the theta So, this constant K instead of defining it to be an absolute constant this is represented as some sort of an Arrhenius form all of you know this from the reaction kinetics that this Arrhenius form of the reaction kinetics which is dependent on the constants and this Q can be represented as some sort of the activation energy which in this case is related to the fractional coverage or the fractional adsorption, q ml in this case is the maximum adsorption capacity and of course, A0 is one constant in this case. So, if you now try to equate these two we get or we try to join all the different components of this equation we get something like this. Now taking logarithmic log on both sides we get this is equal to this is I am substituting the expression of Q in here also which is in terms of Q m l into logarithmic of theta e. Now, for this case the it is considered that when the theta e value is approximately 0.5 or 50 percent of the coverage the above equation this equation here that we just represented can be you know simplified in this form as theta e is equal to a 0 to the power RT by Qml and Ce to the power RT by Qml.



Freundlich isotherm

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$$\frac{\theta_e}{1-\theta_e} = k C_e \qquad K(q) = A_0 e^{q/RT}$$

where $q = -q_{mL} \ln \theta_e$

q_{mL} max. adsorption capacity

$$\frac{\theta_e}{1-\theta_e} = A_0 e^{q/RT} C_e$$

$$\boxed{\ln\left[\frac{\theta_e}{1-\theta_e}\right] = \ln A_0 C_e - \frac{q_{mL}}{RT} \ln \theta_e}$$

when $\theta_e \sim 0.5$, $\theta_e = \underbrace{A_0^{RT/q_{mL}}}_{K_F} C_e^{RT/q_{mL}}$

$$\boxed{\theta_e = K_F C_e^{n}}$$

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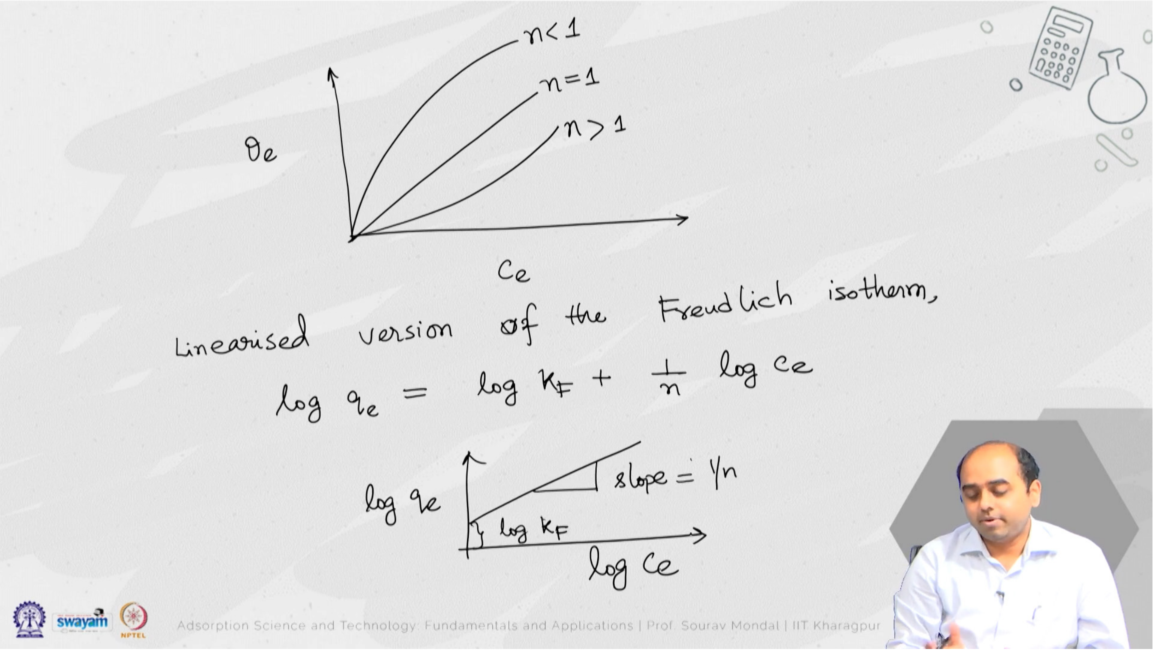
Now, of course, these two coefficients can be represented as like two separate, you know, constants alpha and beta or like KF or something. So, this theta E can be represented as KF C e to the power n. So, where k f represents this constant and n represent this constant and this takes the form of the classic here you know Freundlich isotherm model So, it may be noted that this as you understand that this describes or the basis of this equation is related to the fact that this considers an equilibrium coverage fraction up to 50 percent in this case. So, this whatever the chemical adsorption or physical adsorption up to 50 percent coverage is nicely described by this Freundlich isotherm model. Now, typically the shape of the Freundlich isotherm model, with respect to the different values of n can look something like this.

These are the different possible scenarios with the Freundlich isotherm and one can also work out the you know this linearized version of this Freundlich isotherm. Taking log on both sides as. So, if you if one does a plot of log of q e with respect to the log of C e one would expect to get a straight line and the slope of the straight line you will get as the exponent 1 by n and the and the intercept represents log of k f. So, from the available data of Qe versus Ce one can linearize in this I mean one can fit linear regression and can estimate out these constants. But the same equation also holds true here for even which is also described for the Langmuir that often the errors associated during the measurement gets magnified when you convert either they are reciprocal in the case of Langmuir isotherm, or in the case of the logarithmic value in this case is also magnified and one should be careful in you know manipulating or interpreting the linearized version to for easy calculation of the regression to find out this unknown coefficients of the model. The next model that we are going to talk about is the Redlich Peterson model. So, this is again an empirical model and it is an hybrid version combining both the Langmuir and the Freundlich isotherm. So, this is generally you know applied for both homogeneous and heterogeneous adsorption processes and the generic version or the mathematical form of this RP or this Freundlich Peterson model is a combination of both the Freundlich and the Langmuir version. So, this is a three constant model as you can note.

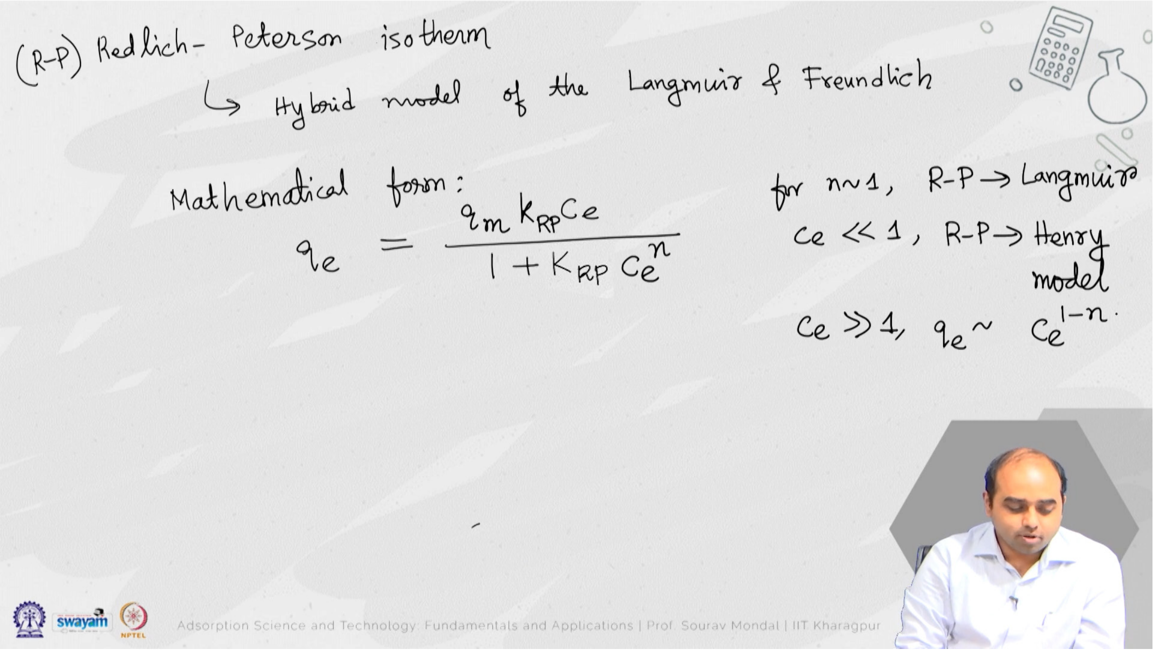


Linearised version of the Freudlich isotherm,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

In the numerator, you have one constant, which is nothing but the product of Qm into k. RP stands for this particular, I mean, this Redlich-Peterson isotherm. And in the denominator, you see that is one particular constant is there and then it is again multiplied with an exponent n. So, of course, you can understand as n tends to 1, this Redlich-Peterson isotherm converts. So, for n close to 1 this RP model you know translates to the Langmuir model.

And whereas, this in the case of low concentration in the case of low concentration or when C e is very small, this RP model falls back to the Henry's or the linear model. When C is very large in that case the RP model switches or translates to some form of the this Freundlich model where Q e is proportional to C e to the power 1 minus n, with some constant factors. So, these are the limiting regimes of this Redlich Peterson model. The next important model which is again an hybrid of this Langmuir and the Freundlich isotherm model is the SIPS isotherm model. This is also a hybrid of Langmuir and Freundlich isotherm.



(R-P) Redlich- Peterson isotherm

↳ Hybrid model of the Langmuir & Freundlich

Mathematical form:

$$q_e = \frac{q_m K_{RP} C_e}{1 + K_{RP} C_e^{n}}$$

for $n \sim 1$, R-P → Langmuir

$C_e \ll 1$, R-P → Henry model

$C_e \gg 1$, $q_e \sim C_e^{1-n}$.

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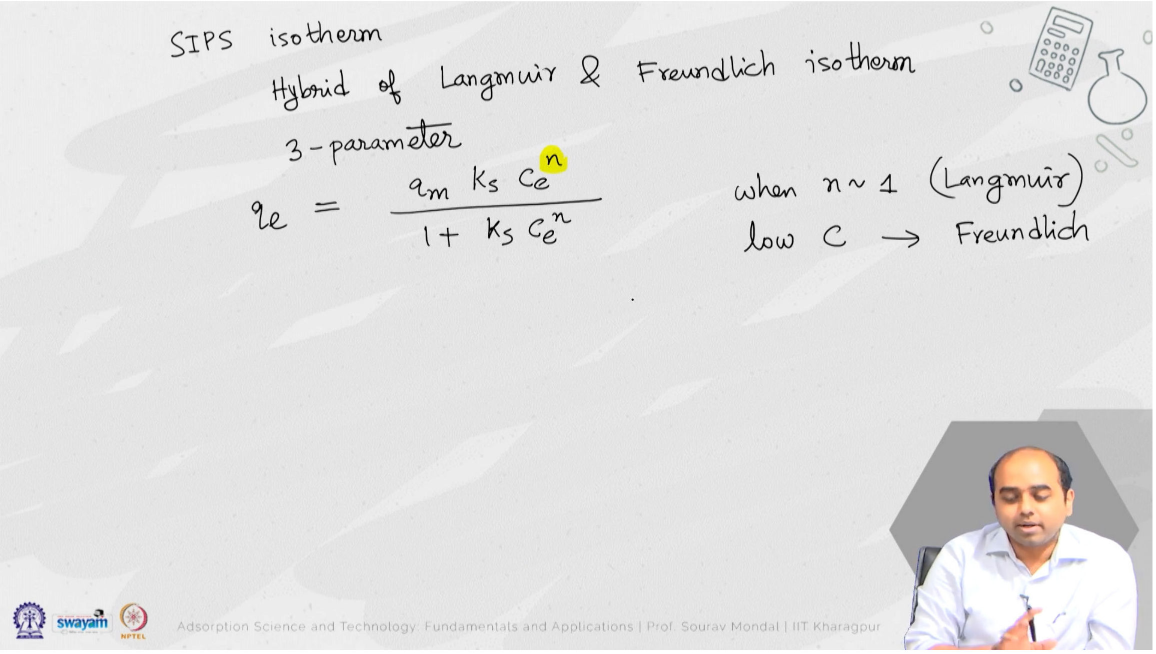
So, this is used to describe both the homogeneous as well as the heterogeneous model. This is also a 3-parameter mathematical function. So, please note that the Langmuir and the Freundlich are all 2-parameter models, whereas SIPS is a 3-parameter model. So, in this case, it is very similar to the Redlich-Peterson model, except that in the numerator you also have that exponent. So here I just try to highlight that the extra addition from the from the Redlich-Peterson model is the presence of the exponent in the numerator of this mathematical equation which makes it different from the Redlich-Peterson model. The SIPS model converts to the as you can understand converts to the Langmuir model when n is equal to the 1 and becomes Freundlich model. So, this is the case when it gets Langmuir type. It becomes Freundlich for low values of low C this gets converted the SIPS model gets converted to the Freundlich version. Interestingly, the SIPS model does not fall back to the Henry's form which is the case with ah Redlich ah Peterson or the RP model at low values of c because of the presence of this exponent m. So, this SIPS model is generally not very useful or very applicable at low concentrations because typically most, molecules in in reality follows this monolayer type behavior or the linear behavior and expresses or you know shows or exhibits a linear regime described by this Henry's law, which is of course, not supported by this SIPS isotherm.



SIPS isotherm

Hybrid of Langmuir & Freundlich isotherm

3-parameter

$$q_e = \frac{q_m K_s C_e^{n}}{1 + K_s C_e^{n}}$$

when $n \sim 1$ (Langmuir)

low C → Freundlich

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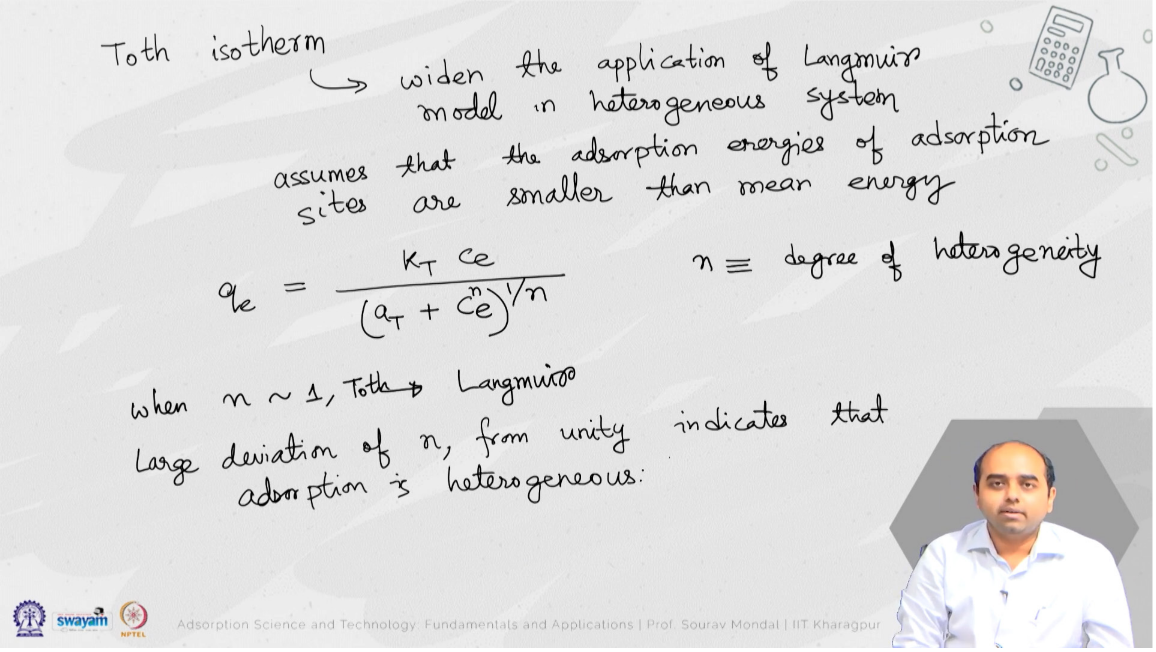
So, this is not particularly very good or applicable for low concentration. Next comes the TOTH isotherm. So, this model is also used to widen this Langmuir application for heterogeneous system. So, this is generally the purpose for which it is evolved is to widen the application of Langmuir isotherm for Langmuir model in heterogeneous systems. So, this particular isotherm assumes that the mean energy, assumes that the adsorption energies of adsorption sites are smaller than the mean energy.

So, the equation for this one is same in the numerator, but the denominator is different So, where this Kt and this you know At both are you know isotherm constant and this particular value of this N represents the degree of heterogeneity. So, this N represents the degree of heterogeneity that is present in this adsorption systems. So, when Z becomes equal sorry when N becomes equal to 1, n is equal to 1 this gets converted the TOTH isotherm gets converted to the Langmuir version. Large deviation of the value of this exponent n from 1 suggest the presence of heterogeneity in the adsorption which is particularly not captured in the Langmuir isotherm. So, large deviation of n from unity indicates that adsorption is heterogeneous or is dominantly heterogeneous.



Toth isotherm

↳ widen the application of Langmuir model in heterogeneous system

assumes that the adsorption energies of adsorption sites are smaller than mean energy

$$q_e = \frac{K_T C_e}{(a_T + C_e^n)^{1/n}}$$

$n \equiv$ degree of heterogenity

when $n \sim 1$, Toth → Langmuir

Large deviation of n, from unity indicates that adsorption is heterogeneous.

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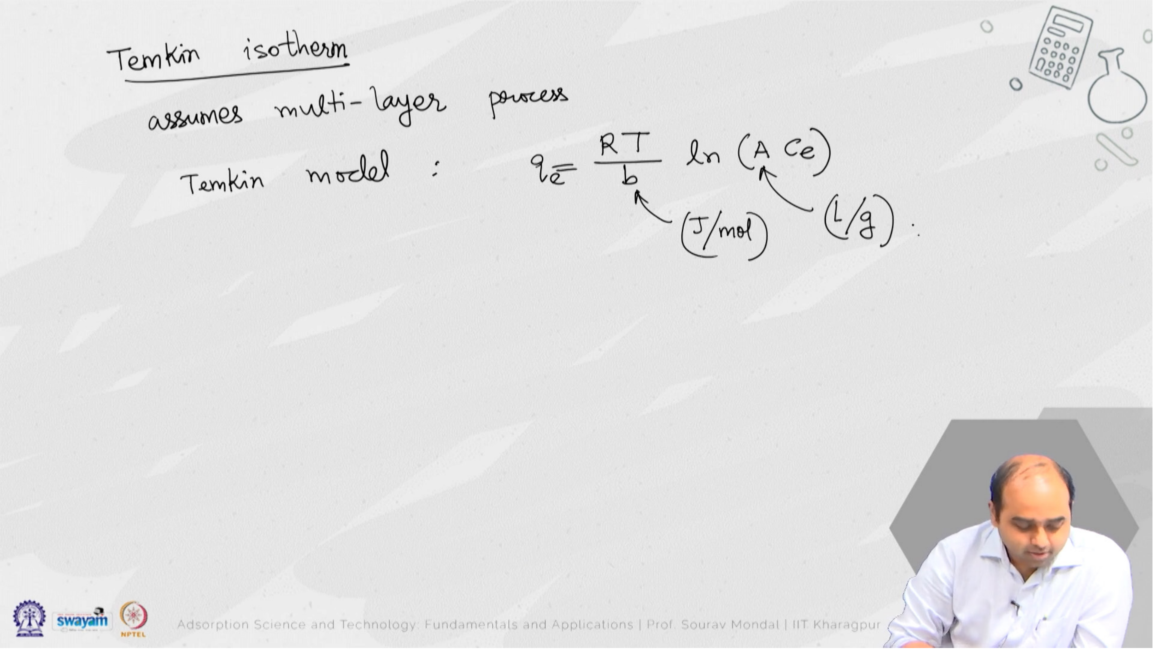
Next, we are going to describe the another important isotherm which is the Temkin isotherm. Temkin isotherm is also a very popular isotherm and this assumes multilayer you know process So, this extremely high and low values of the adsorbate in the liquid phase is generally not very much applicable to be described by this Temkin isotherm. So, that is one sort of limitation for this model. This was derived based on the statistical mechanical expression and this has a you know relation with the Clausius-Clapeyron equation from the thermodynamics which confirmed that the differential heat of adsorption for this was linearly decreasing with increasing coverage or increasing adsorption in this case. So, the mathematical model of the Temkin isotherm is represented like this.



Temkin isotherm

assumes multi-layer process

Temkin model : $q_e = \frac{RT}{b} \ln (A\, C_e)$

(J/mol)

(L/g)

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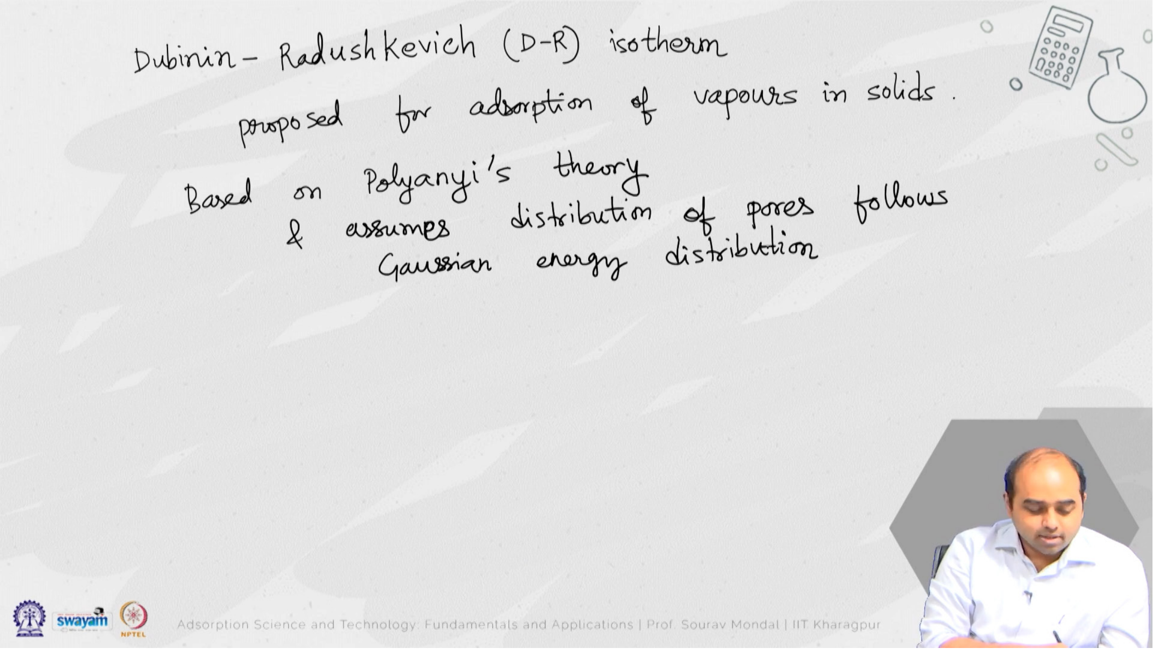
Interestingly the temperature is nicely captured in this model equation itself which is the characteristic feature of this Temkin isotherm. So, this is as you can understand is very relevant for scenarios where there is a wide variation of the adsorption capacities and the adsorption behaviour with respect to temperature Temkin isotherm is very suitable for that purpose. The values a and b are essentially the isotherm constants and you can understand that this this units of b this is in joule per mole and this a is litre per gram. Next we are going to talk about another important isotherm model known as this Dubinin Radushkevich (DR) isotherm. So, this is generally used or it was originally proposed for adsorption of vapour in solids.



Dubinin- Radushkevich (D-R) isotherm

proposed for adsorption of vapours in solids.

Based on Polyanyi's theory

& assumes distribution of pores follows

Gaussian energy distribution

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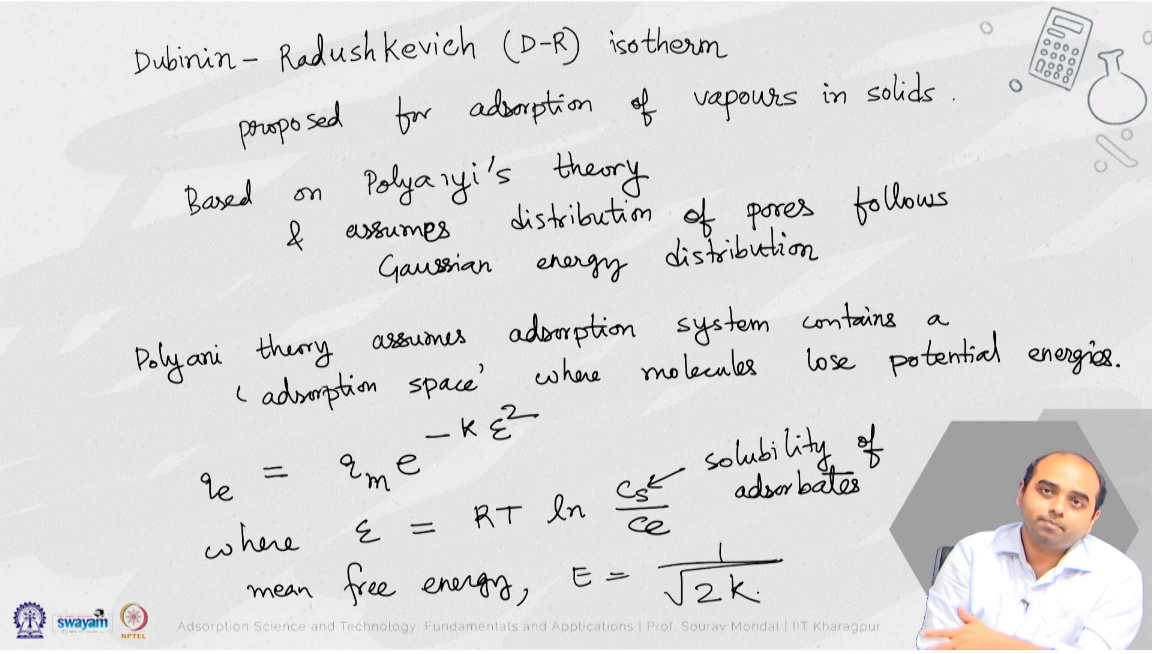
And this is developed in accordance to the Polyani's theory. So, this is based on Polyani's theory and assumes that the distribution of the force present in the adsorbent follows Gaussian energy distribution. So, the Polyani's assumption or the Polyani's theory assumes or considers that all molecules has an adsorption space which covers the adsorption process and the molecules lose potential energy during the process of adsorption. So, the potential energies are generally temperature independent and increase in the species closing to the adsorbent. So, this Polyani's theory assumes adsorption system contains an adsorption space where molecules lose potential energies.

The potential energies I am repeating once again that is it important the potential energies are temperature independent and they increase in the spaces closing to the adsorbent. So, the highest potential energy is reached in the pores or the cracks which is present inside this adsorbent. Now, let us look into the adsorption you know non-linear model equation. So, in this case the Qe is defined as Qm e to the power minus k epsilon square where epsilon is equal to RT ln Cs by Ce. So, here Cs represents the solubility of the adsorbates and Ce represent the concentration of the adsorbates at equilibrium.



Dubinin- Radushkevich (D-R) isotherm

proposed for adsorption of vapours in solids.

Based on Polyanyi's theory
& assumes distribution of pores follows
Gaussian energy distribution

Polyani theory assumes adsorption system contains a
'adsorption space' where molecules lose potential energies.

$$q_e = q_m e^{-K\varepsilon^2}$$

where $\varepsilon = RT \ln \frac{C_s}{C_e}$ ← solubility of adsorbates

mean free energy, $E = \frac{1}{\sqrt{2K}}$

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This model also captures the temperature effects within the isotherm itself. It must be noticed that many a times in various other platforms and in other you know places or resources that E epsilon is incorrectly represented as RT 1 plus the inverse of ah 1 by Ce that is not particularly true and it is only true in special cases where this ratio I mean that you can understand that when Ce is close to Cs this ln can be expanded in the form of ln of 1 plus x format. The mean free energy for this particular you know system can be represented from the this constant of the model in this way. So, this is generally used many a times the free energy is generally used to quantify whether the adsorption or the is dominated by physisorption or chemisorption. Because typically for physisorption the value of the free energy change is within you know 5 to 10 kilo joules per mole whereas, in the case of physisorption it is higher than 10 and go can go all the way up to 30 or 40.

So, with this I would like to close this lecture today and there are there is one more important isotherm which is this Brunner, Emelet and this Teller BET isotherm and that forms the basis of the BET equipment, but that is something we will cover in one of the you know weeks in fact about this BET isotherm and its use and its principle and how it is related to the BET equipment. So, with this I would close this lecture. In the next lecture we are going to talk about some you know small example problems related to modeling of equilibrium systems in this scenario. Thank you. I hope all of you has found this lecture useful.