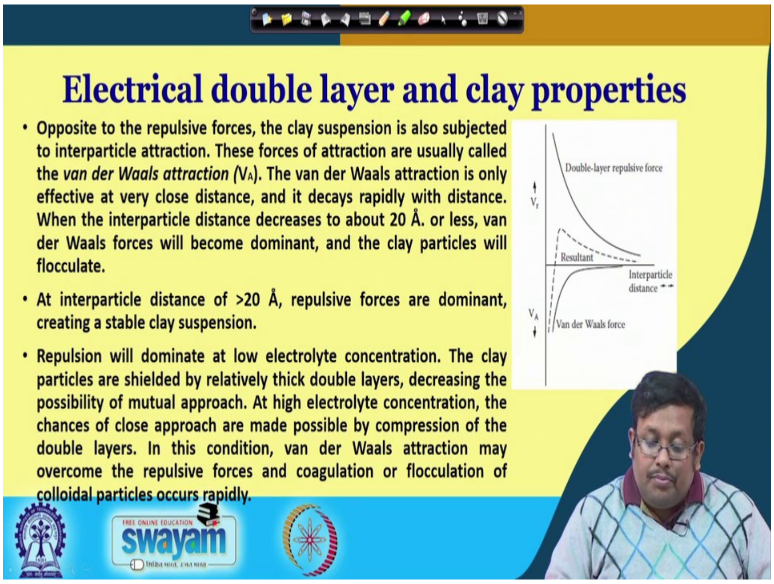
Soil Science and Technology
Prof. SomsubhraChakraborty
Department of Agricultural and Food Engineering
Indian Institute of Technology, Kharagpur

Lecture – 27
Adsorption Isotherms

Welcome, friends to this new lecture of Soil Science and Technology and in this week 6.

(Refer Slide Time: 00:29**)**



Electrical double layer and clay properties

- Opposite to the repulsive forces, the clay suspension is also subjected to interparticle attraction. These forces of attraction are usually called the *van der Waals attraction* (V_A). The van der Waals attraction is only effective at very close distance, and it decays rapidly with distance. When the interparticle distance decreases to about 20 Å. or less, van der Waals forces will become dominant, and the clay particles will flocculate.
- At interparticle distance of >20 Å, repulsive forces are dominant, creating a stable clay suspension.
- Repulsion will dominate at low electrolyte concentration. The clay particles are shielded by relatively thick double layers, decreasing the possibility of mutual approach. At high electrolyte concentration, the chances of close approach are made possible by compression of the double layers. In this condition, van der Waals attraction may overcome the repulsive forces and coagulation or flocculation of colloidal particles occurs rapidly.

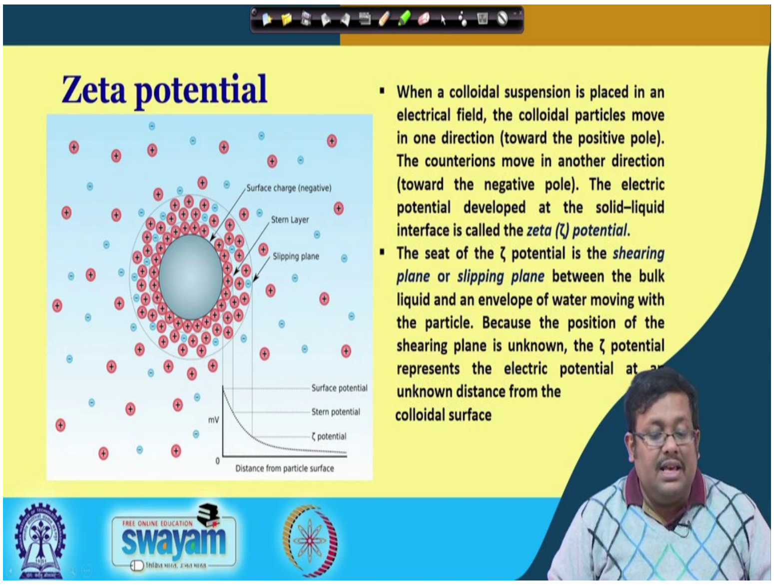
And, today we will try to finish the electrical you know diffuse double layer theories and will move ahead and go to our next topic that is Adsorption Isotherms and then will try to finish that. So, the last lecture we have covered the basics of electrical double layer you know electrical double layer that is diffuse double layer theories and its properties, its assumptions and I talked about you know different diffuse double layer theories like Helmholtz double layer like you know Gouy-Chapman layer and then you know Helmholtz double layer Gouy-Chapman layer then Stern layer.

And, then we talked about what is the basic what are the differences between these three theories and we talked about their assumptions and then we talked about the practical implications of diffuse double layer and its thickness. So, if you remember in the last lecture we have talked about that we know how the thickness of the diffuse double layer is influenced by the valency of the ions as well as the concentration of the electrolytes. And, if you remembered that opposite to default repulsive forces the clay suspension is also subjected to the interparticle attraction we call it van der Waals force and the van der Waal attraction is only effective at very close distance.

And, you know which is less than 20 Armstrong and it decreases we know it decreases rapidly when the interparticle distance goes beyond 20 Armstrong. And, you know the interparticle distance is very important and the repulsion will dominated low electrolyte concentration and the clay particle are shielded by relatively thick double layers and decreasing the possibility of mutual approach. And, remember that at high electrolyte concentration the chances of close approach are made possible by you know compression of the double layer and in this condition van der Waal reduction may overcome the repulsive forces and coagulation and flocculation of the clay particles occurs rapidly.

And, I have told you that this coagulation or flocculation is important soil as far as is soil physical properties concerned because it helps in aggregation as we know as opposed to the dispersion of the clay. At dispersion basically occurs due to the you know you know due to thick diffuse double layer than when the soil is dispersed it creates the unfavourable physical and as well as different other properties for you know soil you know for the growth and germination of the crops.

(Refer Slide Time: 03:30)



Zeta potential

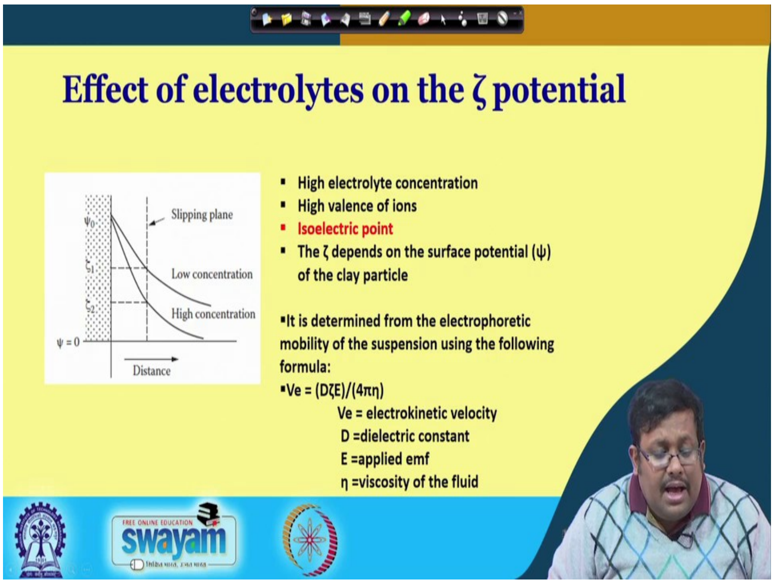
- When a colloidal suspension is placed in an electrical field, the colloidal particles move in one direction (toward the positive pole). The counterions move in another direction (toward the negative pole). The electric potential developed at the solid–liquid interface is called the *zeta (ζ) potential*.
- The seat of the ζ potential is the *shearing plane* or *slipping plane* between the bulk liquid and an envelope of water moving with the particle. Because the position of the shearing plane is unknown, the ζ potential represents the electric potential at unknown distance from the colloidal surface

So, let us move ahead and go to next slide and see what is zeta potential. Now, when a colloidal suspension is placed in a electrical field remember that the colloidal particles move in one direction and towards the positive pole we know that because, they are negatively charged and the counter ions move in another direction we towards the negative pole and the electric potential develops at the solid liquid interface is called zeta potential. And, this zeta potential basically you know the site of the zeta potential is basically is the shearing plane or slipping plane between the bulk liquid and the envelope of water moving with the particle.

So, if you consider this is a particle and there is an envelope of water you can see which is surrounding the soil particles. The slipping plane is basically the plane which is which occurs at the you know at the juncture of this bulk solution, here is a bulk solution in a that is you know envelope of water. So, here you know at the at the junction of the bulk solution and at the you know with the outer we know boundary of the liquid film or envelope, this is called the slipping plane and this slipping plane is a place where, the zeta potential occurs. And, remember that because the position of the shearing plane is unknown and you know the zeta potential you know represents the electric potential at an unknown distance from the colloid surface.

So, we can see here the zeta potential develops at the slipping plane and again the slipping plane is a juncture between the outer boundary of the liquid envelope surrounding and particle and the surrounding bulk solution.

(Refer Slide Time: 05:40**)**



Effect of electrolytes on the ζ potential

- High electrolyte concentration
- High valence of ions
- Isoelectric point
- The ζ depends on the surface potential (ψ) of the clay particle

▪It is determined from the electrophoretic mobility of the suspension using the following formula:

▪$V_e = (D\zeta E)/(4\pi\eta)$

V_e = electrokinetic velocity
D =dielectric constant
E =applied emf
η =viscosity of the fluid

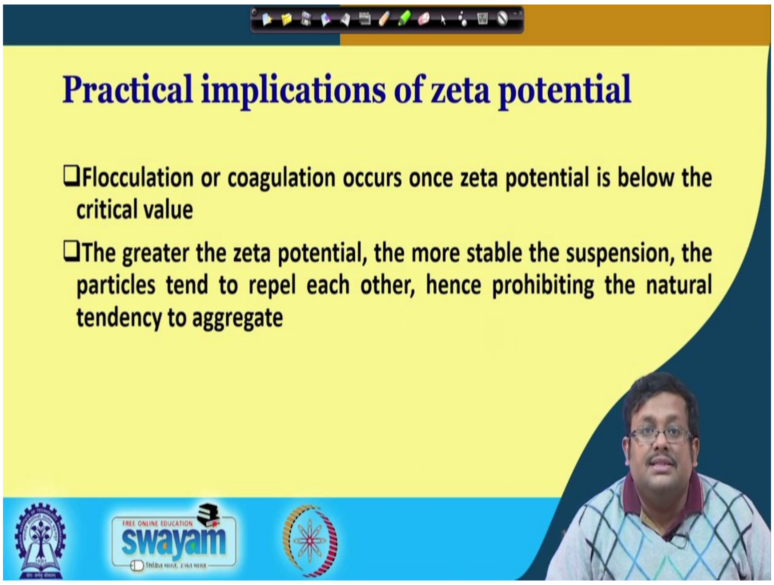
So, let us move ahead and see what are the other features of zeta potential. Now, zeta potential influenced by the high electrolyte concentration; as you remember that when they are high into electrolyte concentration the thickness of the diffuse double diffuse double decreases at the same time due to the thick due to the reduce thickness of the diffuse double also zeta potential also decreases.

So, high electrolyte concentration or high valency finance also decreases this the zeta potential and isoelectric point is the point where zeta potential is critical it is value of 0 and below the below the iso electric point clay particle cannot present as dispersing the medium and they try to flocculate and coagulate and in other words isoelectric point is a pH at which the total surface charge is 0 that is you know. So, this is called the iso electric point. Now, the iso electric point at the critical level below the iso electric point we know the zeta potential reaches you know in certain value where the clay particles are cannot remain further into the solution and they coagulate.

At the zeta potential depends on the surface potential of the clay particles and it is determined from the electrophoretic mobility of the suspension using the following formula where V e equal to you know sorry where Ve equal to D Z E by 4 eta and pi and where Ve is the electro kinetic velocity, D is dielectric constant, E is the applied electromotive force and eta is the viscosity of the fluid. So, by using this formula we can calculate the zeta potential.

So, also a one important thing that you can see here there are two electrolyte you know you know one electrolyte is given here in low concentration another is in a high concentration. So, when there is a high concentration of electrolyte, obviously, the zeta potential decreases. So, highly potential high electrolyte concentration always decreases the zeta potential and helps in coagulation of the clay particles.

(Refer Slide Time: 08:08)

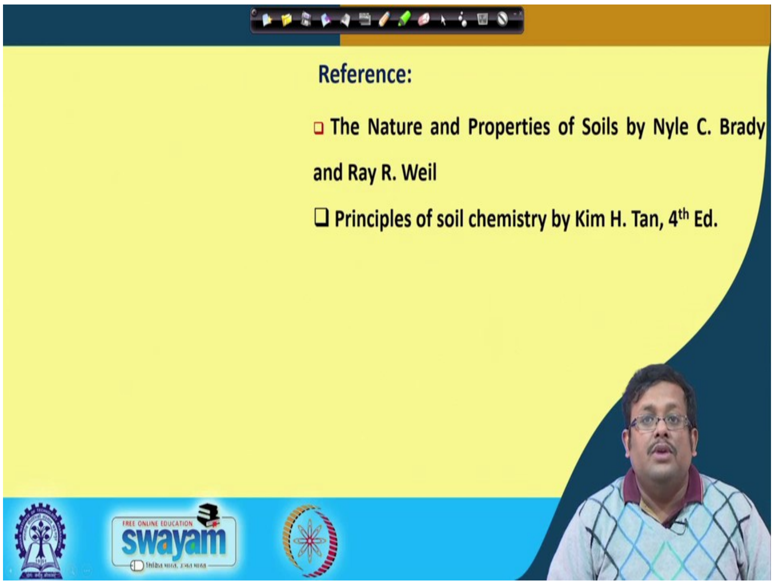


Practical implications of zeta potential

- ❑Flocculation or coagulation occurs once zeta potential is below the critical value
- ❑The greater the zeta potential, the more stable the suspension, the particles tend to repel each other, hence prohibiting the natural tendency to aggregate

So, practical implications of zeta potential flocculation or coagulation occurs when zeta potential is below the critical value. This critical value is called the isoelectric point. And, the greater the zeta potential the more stable the suspension the particle tense to the repel each other hence, prohibiting the natural tendency to aggregate and this repulsion and you know this repulsion and stable suspension is not helpful for the growth of the plan because it creates unfavourable soil physical condition.

(Refer Slide Time: 08:39)

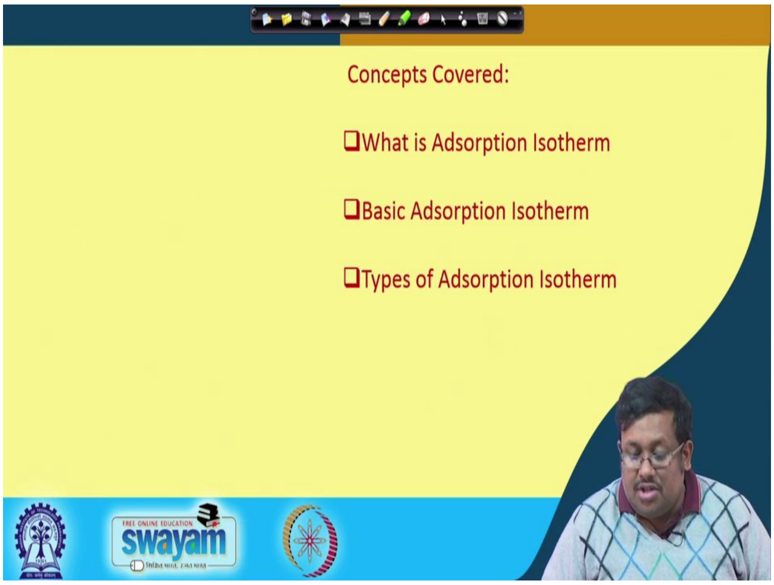


Reference:

- ❑ The Nature and Properties of Soils by Nyle C. Brady and Ray R. Weil
- ❑ Principles of soil chemistry by Kim H. Tan, 4th Ed.

So, we have finished the diffuse double layer theories. Obviously, you can follow these two standard books one is the Nature and Properties of Soil by Nyle C. Brady and Ray R. Weil. And, The Principles of Soil Chemistry by Kim H. Tan, 4th edition and you will have more you know more detail idea about this diffuse double layer while you read these two books in details.

(Refer Slide Time: 09:15)

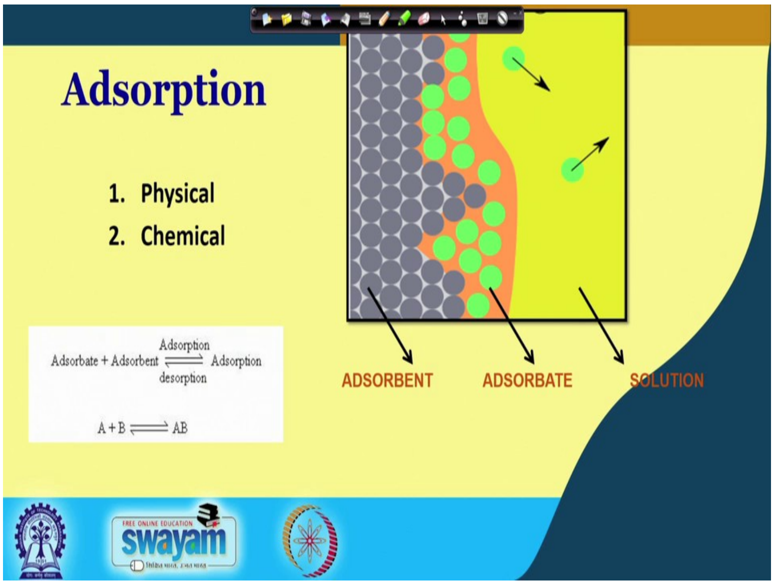


Concepts Covered:

- ☐What is Adsorption Isotherm
- ☐Basic Adsorption Isotherm
- ☐Types of Adsorption Isotherm

So, guys let us move forward and you know start a new topic that is adsorption isotherms. Now, adsorption isotherms is basically deals with adsorption process. Now, we will cover this following concept what is adsorption isotherm and then basic adsorption isotherms and then types of adsorption isotherms.

(Refer Slide Time: 09:23)



Adsorption

1. Physical
2. Chemical

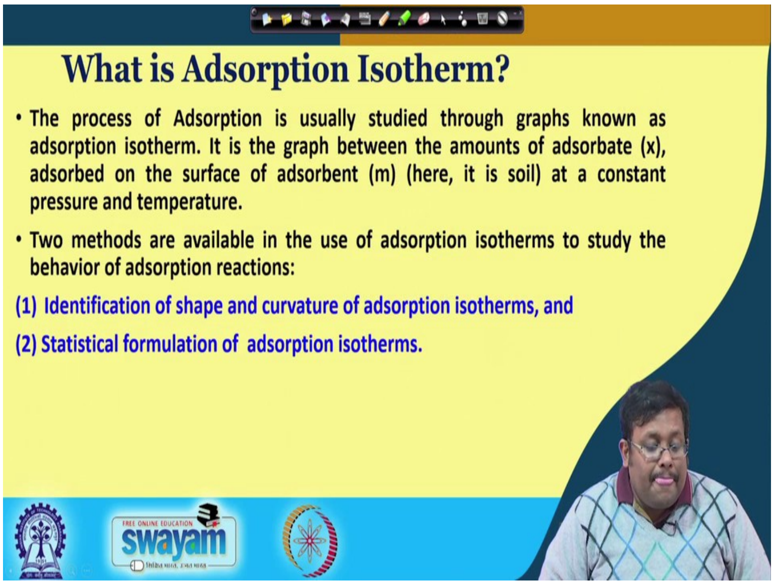
$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

So, what is adsorption? Adsorption can be divided into you know physical adsorption or chemical adsorption. Another name of absorption physical adsorption is physisorpition and chemical adsorption is chemisorption. So, in case of adsorption remember that adsorption is surface phenomena where you know one you know the adsorbate is attached on the surface of the adsorbent and it is a you know it is a reversible. Obviously, as you can see here and adsorbent is the material on which surface adsorption occurs and adsorbent is the material which get absorbed.

So, and also there is a bulk solution. So, this you know this shows in a nutshell about the adsorption process and opposite of adsorption is desorption. Remember that adsorption again is a surface phenomenon it is you know where as absorption which is AB is a intern you know which is in which is not surface phenomenon which is an internal phenomenon and the opposite of adsorption is called desorption. And obviously, in case of adsorption process adsorbate and adsorbent takes part in you know basically reacts with each other.

(Refer Slide Time: 10:43)



What is Adsorption Isotherm?

- The process of Adsorption is usually studied through graphs known as adsorption isotherm. It is the graph between the amounts of adsorbate (x), adsorbed on the surface of adsorbent (m) (here, it is soil) at a constant pressure and temperature.
- Two methods are available in the use of adsorption isotherms to study the behavior of adsorption reactions:

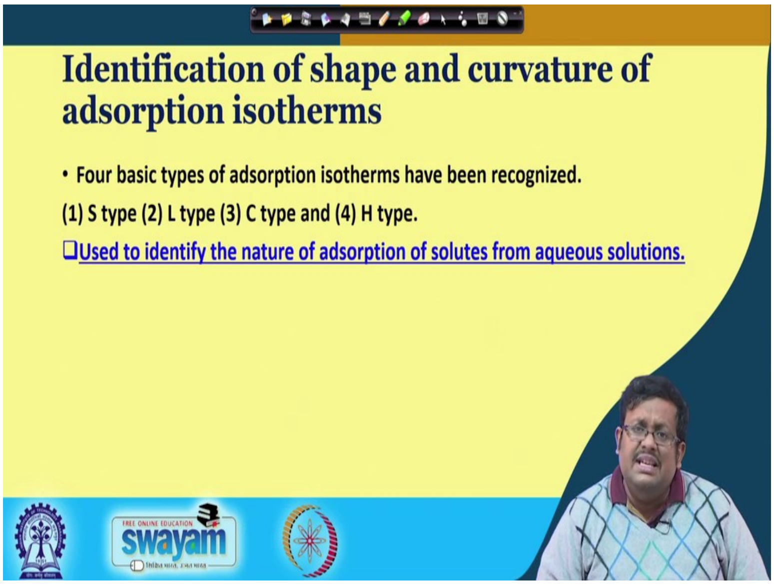
(1) Identification of shape and curvature of adsorption isotherms, and

(2) Statistical formulation of adsorption isotherms.

So, what is adsorption isotherm? Obviously, the process of adsorption is usually studied through graphs known as adsorption isotherms and it is graph between the amount of adsorbate x. And you know adsorbed on the surface of adsorbent m where, in this case we know in our case in case of soil science we consider these adsorbent you know as soil and at a constant pressure and temperature; and, two methods are available. So, adsorption isotherm is basically again showing the you know is the relationship between the amount of adsorbate adsorbed on the surface of the adsorbent and we know at a constant pressure and temperature.

And, two methods are available in the use of adsorption isotherms to study the behaviour of the adsorption isoreaction. First is the identification of the shape and curvature of the adsorption isotherms will see in details and finally, the statistical formulation of adsorption isotherms and the statistical formulation of adsorption isotherms are also called statistical models. So, will discuss them you know in a while.

(Refer Slide Time: 12:00)



Identification of shape and curvature of adsorption isotherms

- Four basic types of adsorption isotherms have been recognized.

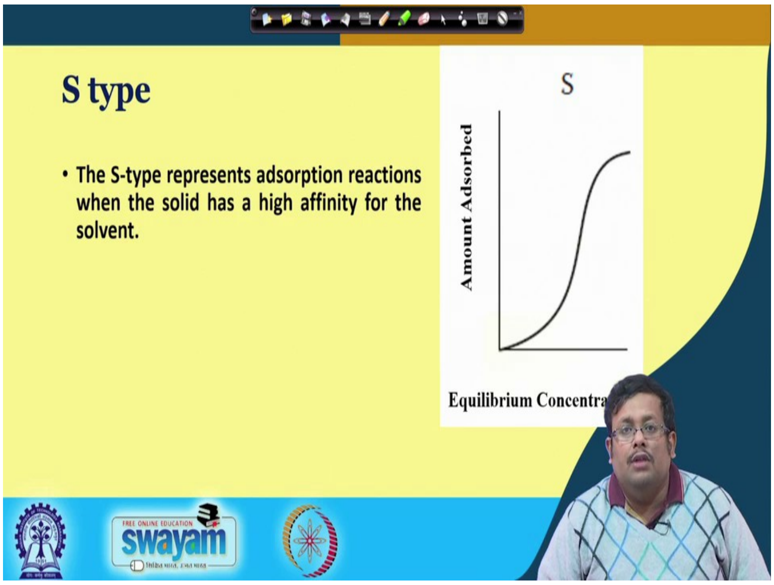
(1) S type (2) L type (3) C type and (4) H type.

❑Used to identify the nature of adsorption of solutes from aqueous solutions.

So, let us first start with the shape and curvature of different adsorption isotherms. Now, identification of shape and curvature of adsorption isotherms is basically focused on four basic types of adsorption isotherms. First of all S type and then L type, then C type and H type and remember that these you know shape and curvature are used to identify the nature of adsorption of solutes from aqueous solution.

So, in this case you know here the adsorbent is basically if you if you remember the difference between adsorbent and adsorbate in our case the adsorbent is soil and adsorbate is a particular molecule which is getting adsorbed on the adsorbent from the solution or soil solution. So, here using this shape and curvature of adsorption isotherms we used to identify the nature and adsorption of solutes from aqueous solution. So, solutes is basically adsorbent. Now, I am the sorry solid is again in our case here the adsorbent is basically soil and adsorbate is basically solute and here is a solution. I hope that now it is clear.

(Refer Slide Time: 13:21)

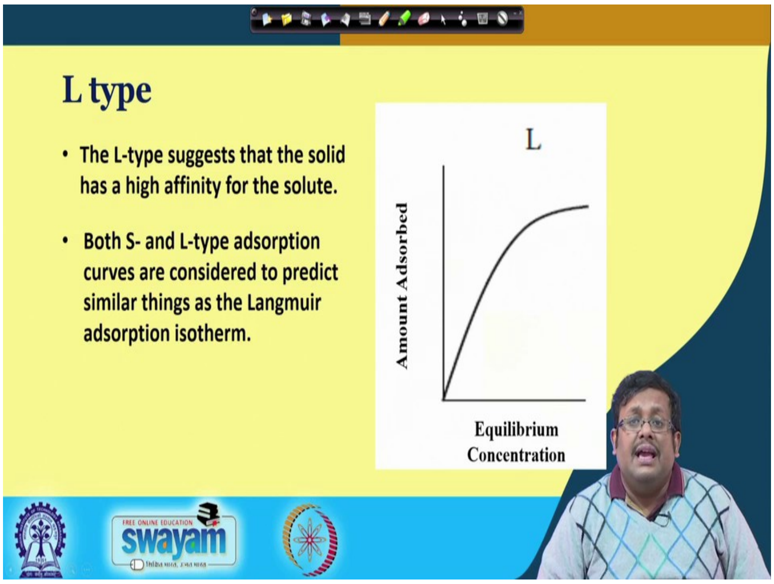


S type

- The S-type represents adsorption reactions when the solid has a high affinity for the solvent.

So, let us move ahead and see what is S type. Now, S type is represent the adsorption reaction when the solid has a high affinity for the solvent. See you can see this shows the relationship between equilibrium concentration and amount adsorbed. See you can see there is an S shape curve and these S shape curve basically denote the with the that the solid has a high affinity for the solvent.

(Refer Slide Time: 13:49)



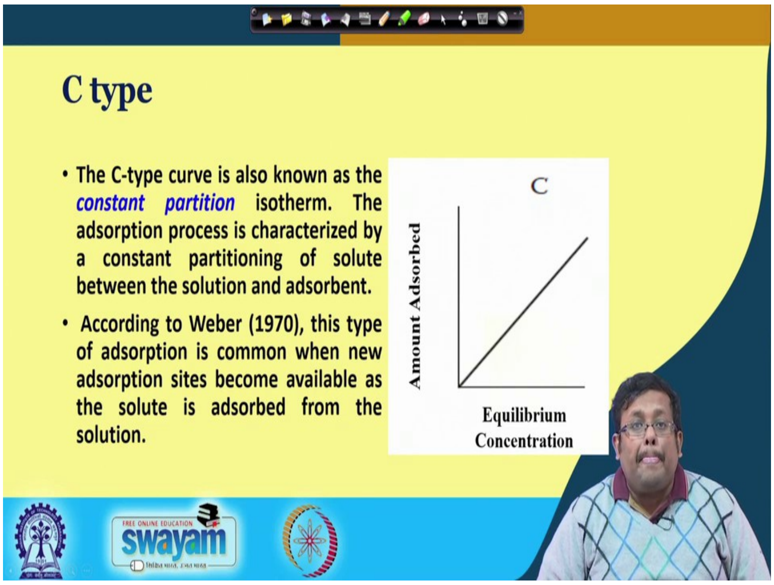
L type

- The L-type suggests that the solid has a high affinity for the solute.
- Both S- and L-type adsorption curves are considered to predict similar things as the Langmuir adsorption isotherm.

And secondly, there is an L type adsorption isotherm. These L type suggests that solid has a high affinity for the solute. So, in case of S type the solute the solid has a high affinity for the for the solid has high affinity for the solvent. However, in case of L type the solute has high affinity for the solute. So, this is an S type and this is again the L type. So, both S type and L type adsorption curves are considered to predict similar things as the Langmuir adsorption isotherm. We will cover the Langmuir adsorption isotherm when we will discuss about the different statistical models of adsorption isotherms later on. But, just remember that this S type and L type adsorption curves are considered to predict similar things as Langmuir adsorption isotherm.

So, again S type where when the solid has high affinity for the solvent and L type when the solid has high affinity for the solute.

(Refer Slide Time: 14:47)



C type

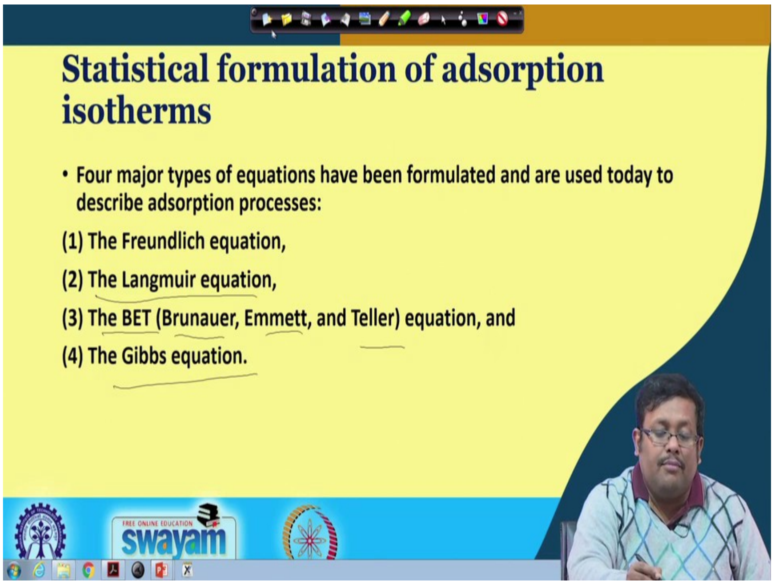
- The C-type curve is also known as the *constant partition* isotherm. The adsorption process is characterized by a constant partitioning of solute between the solution and adsorbent.
- According to Weber (1970), this type of adsorption is common when new adsorption sites become available as the solute is adsorbed from the solution.

So, what is C type? Now, C type curve is also known as the constant partition isotherm. Now, you can see there is a straight line between the equilibrium concentration and amount adsorbed. So, the C type curve is also known as the constant partition isotherm and the adsorption process is characterized by a constant partitioning of solute between the solution and the adsorbent. And, remember that according to Weber scientist this type of adsorption is common when new adsorption sites become available as the solute is adsorbed from the solution.

So, again this S type and L type we already covered. Now, C type is called the constant partition isotherms and the adsorption process here in case of C type is basically characterized by a constant partitioning of the solute between the solution and the adsorbent or in our case it is soil finally, the H type adsorption isotherm. Now, the H type curve also known as the high affinity curve represents adsorption reaction when the solute has a high affinity for the solid. Here remember that solute has a high affinity for the solid in case of S type solid has a high affinity for the solvent, in case of L type solid has a high affinity for the solute. However, in case of H type the solute has a high affinity for the solid.

Now, this type of curve is considered a special type of L curve. Obviously, it is a modification of the L type curve and the entire solution the solute is often completely adsorbed and no measurable amount is left into solution. So, it basically takes this type of form in case of H type.

(Refer Slide Time: 16:40**)**



Statistical formulation of adsorption isotherms

- Four major types of equations have been formulated and are used today to describe adsorption processes:

(1) The Freundlich equation,

(2) The Langmuir equation,

(3) The BET (Brunauer, Emmett, and Teller) equation, and

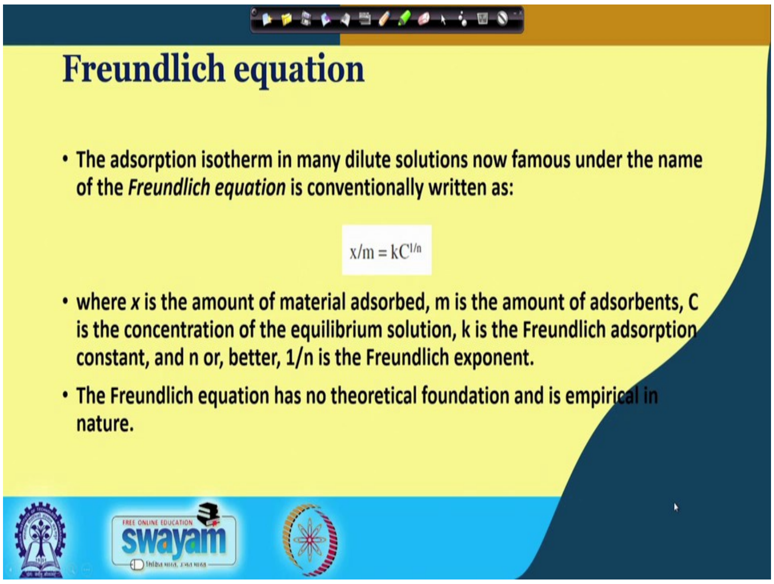
(4) The Gibbs equation.

So, we covered the basic curvature and basic shape of adsorption isotherms you know S type, L type, C type and H type. Let us let us let us see what are the different statistical formulation of adsorption isotherms or in other words what are this different statistical models of adsorption isotherms. So, four major types of equations have been formulated and are used today to describe the adsorption process.

So, these four equations or models are the most you know common you know forms of adsorption isotherms which scientist use nowadays we call it first of all the Freundlich equation and or the Freundlich you know adsorption isotherm, second is a Langmuir equation, third is a BET equation BET comes from three scientist name that is Brunauer, Emmett and Teller equation and finally, that Gibbs equation.

So, we will cover them one by one. So, let us start with a Freundlich equation.

(Refer Slide Time: 17:40)



Freundlich equation

- The adsorption isotherm in many dilute solutions now famous under the name of the *Freundlich equation* is conventionally written as:

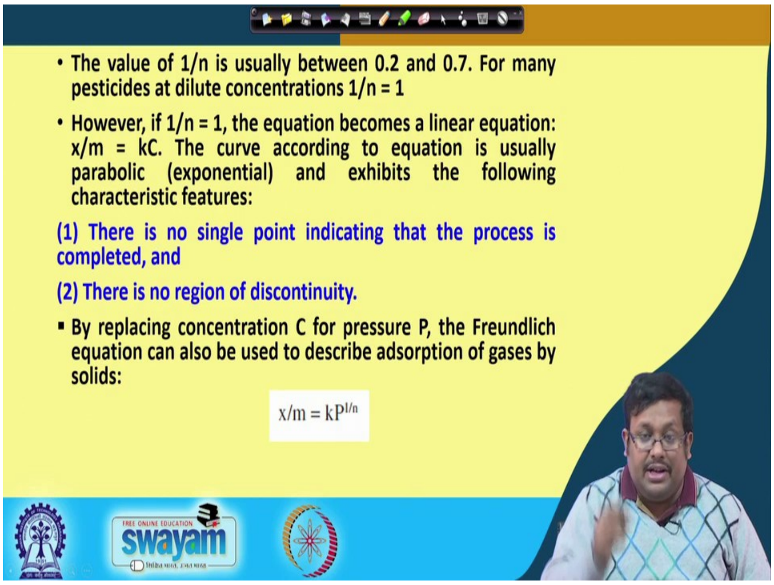
$$x/m = kC^{1/n}$$

- where *x* is the amount of material adsorbed, m is the amount of adsorbents, C is the concentration of the equilibrium solution, k is the Freundlich adsorption constant, and n or, better, 1/n is the Freundlich exponent.
- The Freundlich equation has no theoretical foundation and is empirical in nature.

Now, in case of Freundlich equation the adsorption isotherm in many dilute solution now the famous under the name of the Freundlich equation and is conventionally we write this Freundlich equation as x over m equal to kC to the power 1 by n, where this x is basically the amount of material adsorbed, m is the amount of adsorbent in our case it is soil C is the you know concentration of the equilibrium solution. And, k is the Freundlich adsorption you know Freundlich adsorption constant and n or in other words 1 by n is a basically the Freundlich exponent.

The Freundlich equation obviously, has no theoretical foundation and is purely empirical in nature remember that. So, we have now we have seen the basic you know form of Freundlich equation, let us let us move ahead and see what are the physical interpretation.

(Refer Slide Time: 18:44)



- The value of 1/n is usually between 0.2 and 0.7. For many pesticides at dilute concentrations 1/n = 1
- However, if 1/n = 1, the equation becomes a linear equation: x/m = kC. The curve according to equation is usually parabolic (exponential) and exhibits the following characteristic features:

(1) There is no single point indicating that the process is completed, and

(2) There is no region of discontinuity.

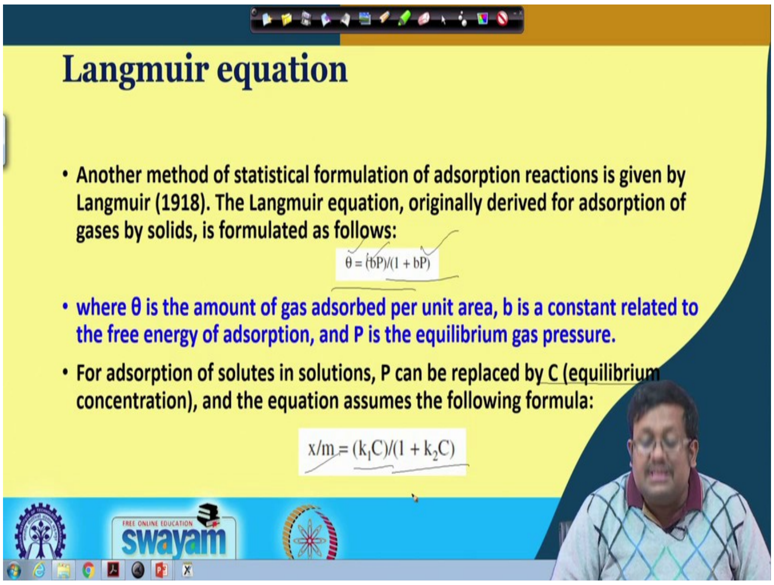
- By replacing concentration C for pressure P, the Freundlich equation can also be used to describe adsorption of gases by solids:

$$x/m = kP^{1/n}$$

Now, remember that the value of 1 by n or in other words the Freundlich exponent is usually between 0.2 to 0.7 and for many pesticides at dilute concentration 1 by n equals to 1. So however, if 1 by n equals to 1 the equation becomes a linear equation because x by m equal to kC where you know the power 1 by n becomes equal to 1. So, the curve according to the equation is usually parabolic which is exponential and exhibit the following characteristic features. First of all there is no single point indicating the process is completed and there is no region of discontinuity. So, these two important assumption.

So, again the Freundlich adsorption isotherms when the Freundlich adsorption you know Freundlich exponent that is 1 by n becomes 1, it becomes you know it becomes a linear equation that is x by m equal to kC. However, the curve according to the equation is usually parabolic you know exponential in nature an exhibits the following two assumptions, characteristic features. But so, by replacing the concentration C for pressure P, obviously, the Freundlich equation can also be used to describe adsorption of gases by the solids. So, we just have to we just have to replace the C by this pressure P. So, basically it will also you know it will be also be applicable for the adsorption of the gases by the solid. So, adsorption of the gases by the solid also follows the Freundlich equation.

(Refer Slide Time: 20:28)



Langmuir equation

- Another method of statistical formulation of adsorption reactions is given by Langmuir (1918). The Langmuir equation, originally derived for adsorption of gases by solids, is formulated as follows:

$$\theta = (bP)/(1 + bP)$$

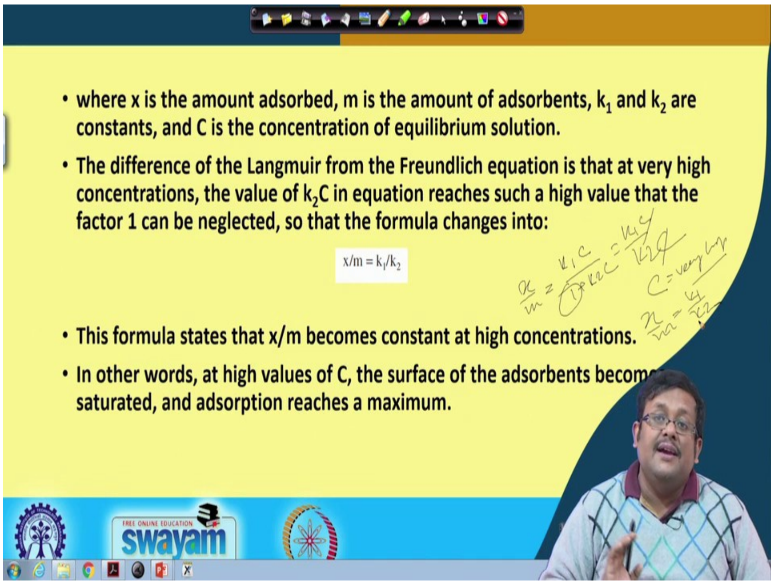
- where θ is the amount of gas adsorbed per unit area, b is a constant related to the free energy of adsorption, and P is the equilibrium gas pressure.
- For adsorption of solutes in solutions, P can be replaced by C (equilibrium concentration), and the equation assumes the following formula:

$$x/m = (k_1C)/(1 + k_2C)$$

So, let us move ahead and see what is Langmuir equation now another method of statistical formulation of adsorption reaction is given by Langmuir in 1918 and the Langmuir equation originally derived for the adsorption of gases by solids is formulated as follows. Obviously, theta equal to bP theta equal to bP by 1 plus bP where theta is the amount of gas adsorbed per unit area b is the constant related to the free energy of adsorption and obviously, P P equals to equilibrium gas pressure.

So, basically it was applied originally to applied for the adsorption of gases by the solid. However, we can modify it for you know in case of solid in case of solute solid interaction also adsorption also. So, for adsorption of solids into the solution P can be replaced by C which is equilibrium concentration of solute in the solution and the equation assumes the following formula where x by m just like the Langmuir equation k 1 C by 1 plus k 2 C and here remember that this is a basic form of the Langmuir equation.

(Refer Slide Time: 21:40)



- where x is the amount adsorbed, m is the amount of adsorbents, k_1 and k_2 are constants, and C is the concentration of equilibrium solution.
- The difference of the Langmuir from the Freundlich equation is that at very high concentrations, the value of k_2C in equation reaches such a high value that the factor 1 can be neglected, so that the formula changes into:

$$x/m = k_1/k_2$$

$$\frac{x}{m} = \frac{k_1 C}{\boxed{1} + k_2 C} = \frac{k_1 \cancel{C}}{k_2 \cancel{C}}$$

C = very high

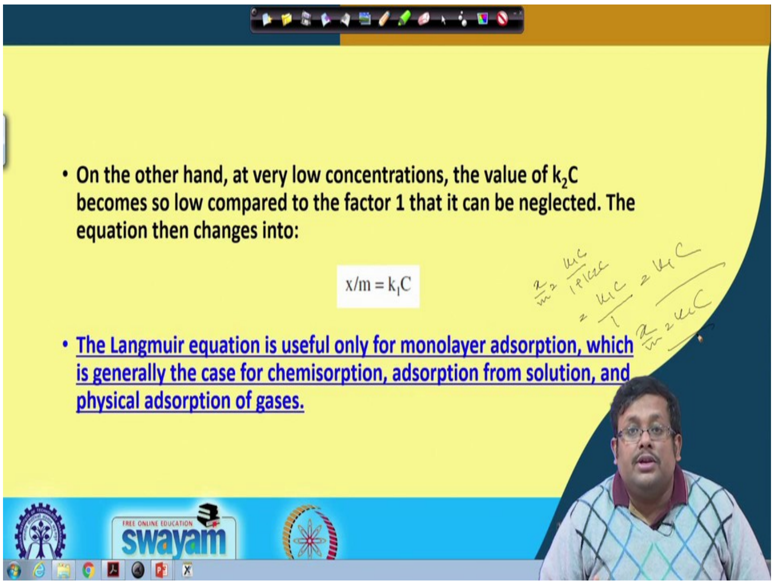
$$\frac{x}{m} = \frac{k_1}{k_2}$$

- This formula states that x/m becomes constant at high concentrations.
- In other words, at high values of C, the surface of the adsorbents becom saturated, and adsorption reaches a maximum.

However, the x is a obviously, the similarly just like just like the Langmuir equation x is the amount adsorbed m is the amount of adsorbent and k 1 and k 2 are the constant and C is the concentration of equilibrium solution; this far you know these are fine. So, remember that the differences of the Langmuir from the Freundlich is that at very high concentration the value of k 2 C, this term k 2 C in equation reaches such a high value that the factor 1 can be neglected.

So, we know that x by m equal to k 1 C plus 1 by k 2 C. So, when the C is very very high very high basically what happens this one we can neglect it. So, basically the equation becomes k 1 C by k 2 C. So, obviously, is become x by m equal to k 1 by k 2. So, this formula shows that that x by m becomes constant at high concentration. So, in other words at high value of C the surface of the adsorbent become saturated and adsorption reaches a maximum. So, this is one implication of this Langmuir equation.

(Refer Slide Time: 23:10)



- On the other hand, at very low concentrations, the value of k_2C becomes so low compared to the factor 1 that it can be neglected. The equation then changes into:

$$x/m = k_1C$$

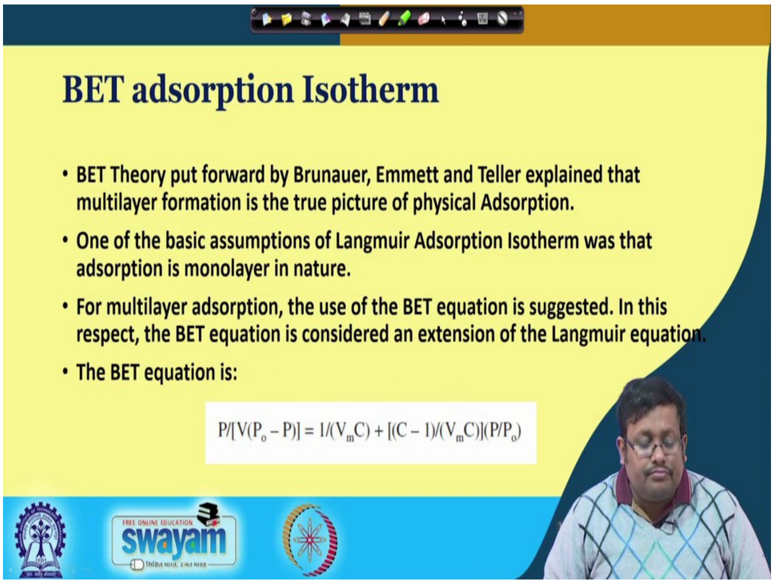
$$\frac{x}{m} = \frac{k_1C}{1+k_2C} = \frac{k_1C}{1} = k_1C$$

$$\frac{x}{m} = k_1C$$

- The Langmuir equation is useful only for monolayer adsorption, which is generally the case for chemisorption, adsorption from solution, and physical adsorption of gases.

However, on the other hand at a very low concentration at a very low concentration the value of k 2 C becomes so low that compared to the factor 1 that it can be neglected. So, then equation turns into, obviously, we know that x by m equal to k 1 C plus 1 by k 2 C. So, here it will you know the value of k 2 C becomes so low so, we know the factor k 2 C can be neglected. So, basically it will be k 1 C, so, the equation change into x by m equal to k 1 C. So, the Langmuir equation is useful remember for monolayer adsorption which is generally in case of chemisorption or chemical adsorption and adsorption for the solution and physical adsorption of the gases.

(Refer Slide Time: 24:14)



BET adsorption Isotherm

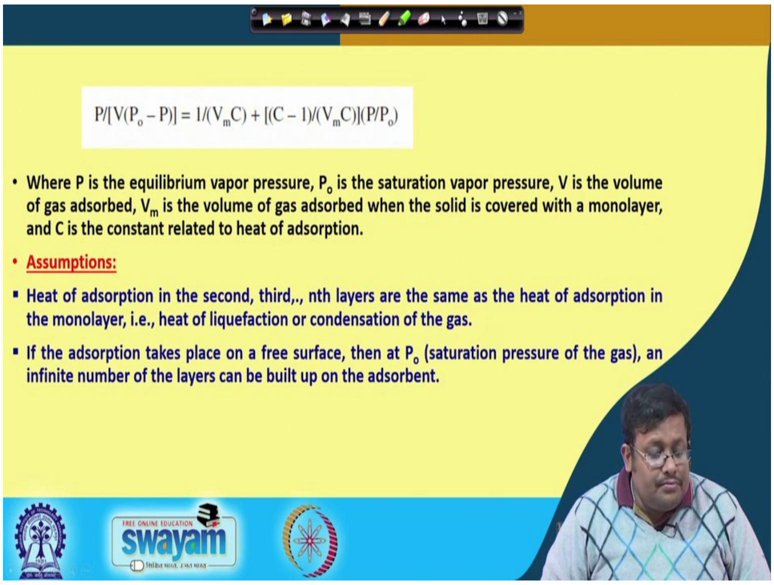
- BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical Adsorption.
- One of the basic assumptions of Langmuir Adsorption Isotherm was that adsorption is monolayer in nature.
- For multilayer adsorption, the use of the BET equation is suggested. In this respect, the BET equation is considered an extension of the Langmuir equation.
- The BET equation is:

$$P/[V(P_o - P)] = 1/(V_mC) + [(C - 1)/(V_mC)](P/P_o)$$

So now, you have know idea about the Langmuir equation and Freundlich equation so, let us go ahead and see what is BET adsorption isotherm. Now, BET theory put forward by these three scientists Brunauer, Emmett and Teller explained that multilayer formation is the true picture of the physical adsorption. Now, one of the basic assumption of Langmuir adsorption isotherm was that adsorption is a monolayer in nature.

However, this BET assume that there are multilayer adsorption you know multilayer adsorption is possible. So, for multilayer adsorption the use of BET equation is suggested and in this respect the BET equation is considered as an extension of the Langmuir equation. It is considered as a extension of Langmuir equation and the BET equation you can see this is the formula of the BET equation.

(Refer Slide Time: 25:05)



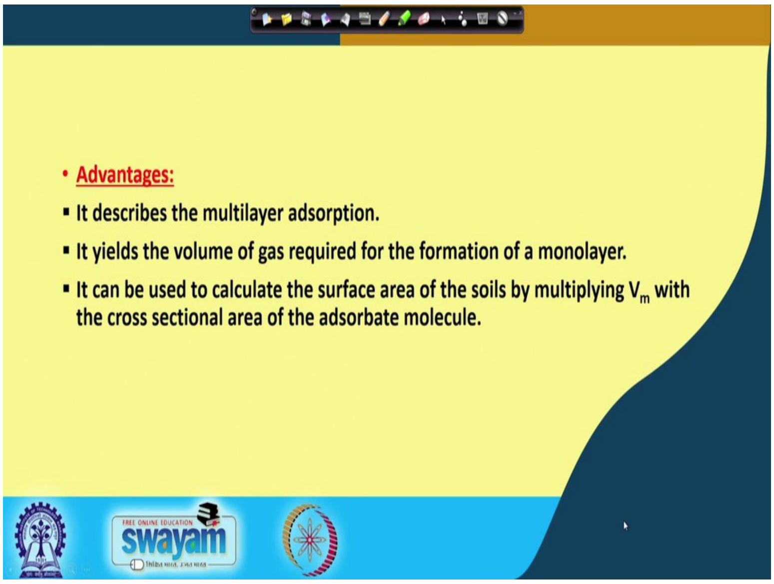
$$P/[V(P_o - P)] = 1/(V_mC) + [(C - 1)/(V_mC)](P/P_o)$$

- Where P is the equilibrium vapor pressure, P_o is the saturation vapor pressure, V is the volume of gas adsorbed, V_m is the volume of gas adsorbed when the solid is covered with a monolayer, and C is the constant related to heat of adsorption.
- Assumptions:
- Heat of adsorption in the second, third,., nth layers are the same as the heat of adsorption in the monolayer, i.e., heat of liquefaction or condensation of the gas.
- If the adsorption takes place on a free surface, then at P_o (saturation pressure of the gas), an infinite number of the layers can be built up on the adsorbent.

So, let us go ahead and see what are the meaning of these terms. So, in this BET equation expression P is the equilibrium vapour pressure, P 0 is a saturation vapour pressure, V is the volume of gas adsorbed, V m is the volume of gas adsorbed when the solid is converted with a monolayer and C is the constant related to the heat of adsorption. So, this is basically the, that the equation of BET of the BET isotherm and these are the meaning of the individual corporate.

Now, what are the assumption? Now, the assumption of BET equation is the heat of adsorption in the second third and n-th layer are the same as the heat of adsorption in the mono layer that is heat of liquefaction or condensation of the gas. And, secondly, the adsorption takes place on a free surface than at P 0 that is saturation pressure of the gas at infinite number of the layers can be built up on the adsorbent. So, these two are assumption basic assumptions of the BET equation.

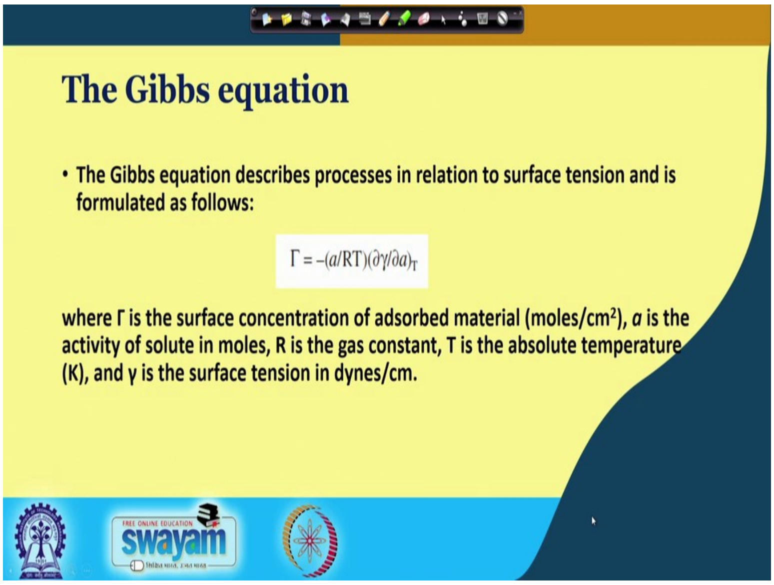
(Refer Slide Time: 26:11)



- **Advantages:**
  - It describes the multilayer adsorption.
  - It yields the volume of gas required for the formation of a monolayer.
  - It can be used to calculate the surface area of the soils by multiplying V_m with the cross sectional area of the adsorbate molecule.

So, what are the advantages of the BET equation? Obviously, it describes the multilayer adsorption and it yields the volume of gas required for the formation of the mono layer and it can be used to calculate the surface area of the soil by multiplying V m with the cross sectional area of the adsorbate molecules. So, these are the three advantages of this BET equation.

(Refer Slide Time: 26:38)



The Gibbs equation

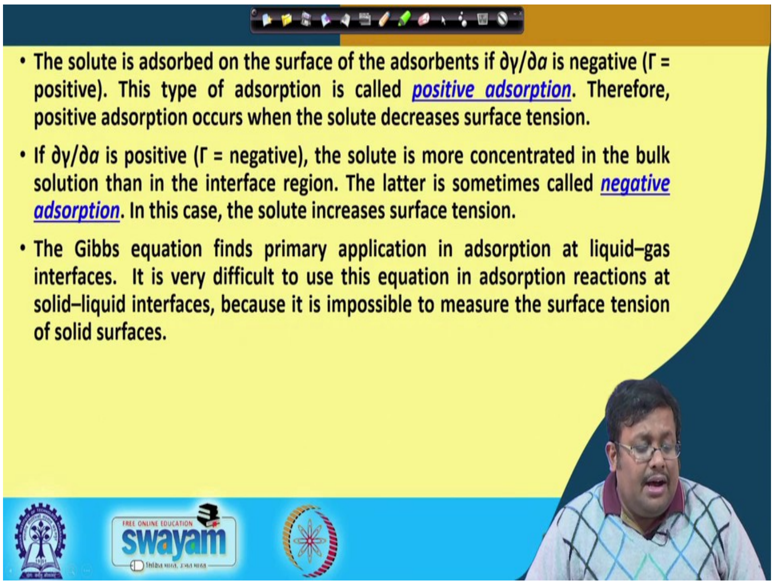
- The Gibbs equation describes processes in relation to surface tension and is formulated as follows:

$$\Gamma = -(a/RT)(\partial\gamma/\partial a)_T$$

where Γ is the surface concentration of adsorbed material (moles/cm^2), a is the activity of solute in moles, R is the gas constant, T is the absolute temperature (K), and γ is the surface tension in dynes/cm.

Finally, the Gibbs equation the Gibbs equation describes the processes in relation to surface tension and it is formulated as follows: where is tau equal to minus a over RT and then d gamma by da subscript T, where tau is surface concentration of adsorbed material in moles per square centimetre. And a is the activity of the solute in mole in moles and R is the you know is the gas constant you know that, T is absolute temperature in Kelvin and you know the gamma is the surface tension in dynes per centimetre.

(Refer Slide Time: 27:23)



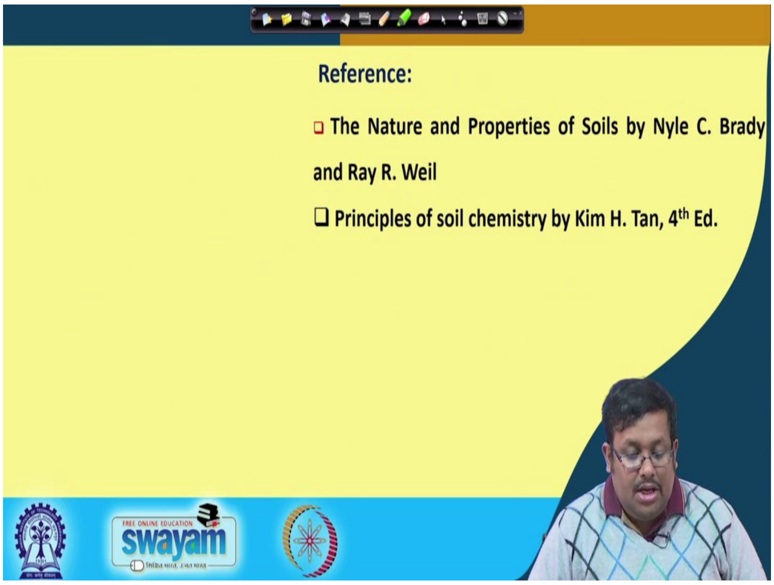
- The solute is adsorbed on the surface of the adsorbents if $\partial\gamma/\partial a$ is negative (Γ = positive). This type of adsorption is called *positive adsorption*. Therefore, positive adsorption occurs when the solute decreases surface tension.
- If $\partial\gamma/\partial a$ is positive (Γ = negative), the solute is more concentrated in the bulk solution than in the interface region. The latter is sometimes called *negative adsorption*. In this case, the solute increases surface tension.
- The Gibbs equation finds primary application in adsorption at liquid–gas interfaces. It is very difficult to use this equation in adsorption reactions at solid–liquid interfaces, because it is impossible to measure the surface tension of solid surfaces.

So, this Gibbs equation takes this form and the solute is adsorbed when the surface of the adsorbent is d gamma by da is negative. So, if you consider if you if you remember this a negative term. So, if this d gamma by d a which is this term is negative. So, ultimately tau is positive. So, this type of adsorption we call it positive adsorption, when the tau is positive when the you know it is called the positive adsorption.

So therefore, positive adsorption occurs when the solute decreases surface tension, remember that. Now, what is negative adsorption negative adsorption is just opposite. So, when the d gamma by d a is positive delta gamma by delta a is positive that means, that tau is negative. So, the solute is more concentrated in the bulk solution that in the interface region. So, in this just opposite to the positive adsorption and the latter you know it is called that negative adsorption and in this case, solute increases the surface tension.

So, in case of positive adsorption solute decreases the surface tension in case of negative adsorption solute decrease increases the surface tension and the Gibbs equation finds primary application in adsorption at liquid gas interface, obviously, and it is very very difficult to use this equation for in adsorption reaction at solid liquid interface because it is impossible to measure the surface tension of the solid interface or solid surface. It is easy to measure the surface tension the liquid surface. However, it is impossible to measure the you know surface tension of solid surface. So, that is why the Gibbs equation is applicable for in adsorption at liquid gas interface.

(Refer Slide Time: 29:06)



Reference:

- ❑ The Nature and Properties of Soils by Nyle C. Brady and Ray R. Weil
- ❑ Principles of soil chemistry by Kim H. Tan, 4th Ed.

So, guys we have completed this adsorption isotherms and their basic you know their curvature and the shape and the statistic four statistical models of adsorption isotherms. Adsorption isotherm is a very very important when there is a adsorption of solutes from the bulk soil solution to the you know soil solids or the clay surfaces.

So, it is very very important. Please read this book again the Nature and Properties of soils by Nyle C. Brady and Principle of Soil Chemistry by Kim H. Tan, fourth edition to get more thorough knowledge of this adsorption process. Obviously, we cannot complete all the you know physical and chemical you know you know physical and chemical forces which are responsible for different types of adsorption. So, I request you to go through these books in more details to learn in details about different types of adsorption isotherms.

But, however, I have you know I hope that you have now got basic idea about the adsorption isotherms. So, we are going to finish this lecture and the next lecture will start from the soil acidity and different other problematic soils.

Till then, thank you.