Soil Science and Technology
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Lecture – 26
Diffuse Double Layer

Welcome, friends to this new week of lectures for Soil Science and Technology and we will start with this, we will start this week with the topic that is Diffuse Double Layer theories. And so, this is very important for different soil physical and chemical properties and we will discuss why.

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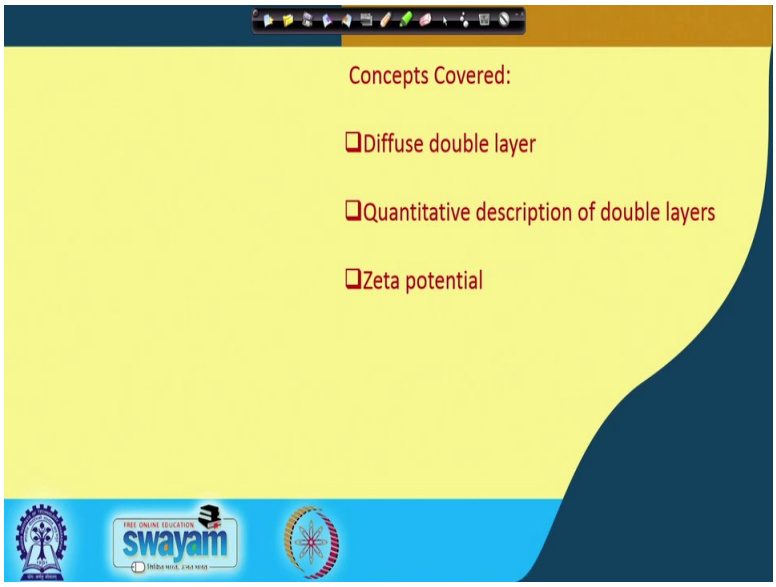

And, we will probably will cover these concepts. For example, what is diffuse double layer, what are the different types of diffuse double layers and what is quantitative description of double layers and then we will talk about zeta potential iso electric points on all these things.

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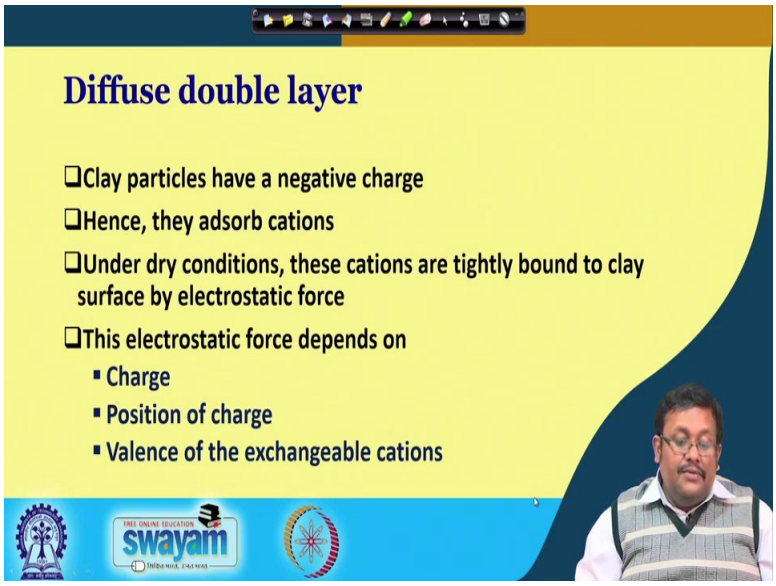

So, let us start with the diffuse double layer. Now, diffuse double layer is basically you know that all the clay particles and negative charge because of either you know iso most of the time this because of isomorphous substitution. So, they can adsorb cations. So, as a result of the adsorption of the cation under dry conditions this cations are tightly bound to clay surface by electrostatic force and this electrostatic force depends on charge, position of charge and valence of exchangeable cations. So, these three are important factors for electrostatic force.

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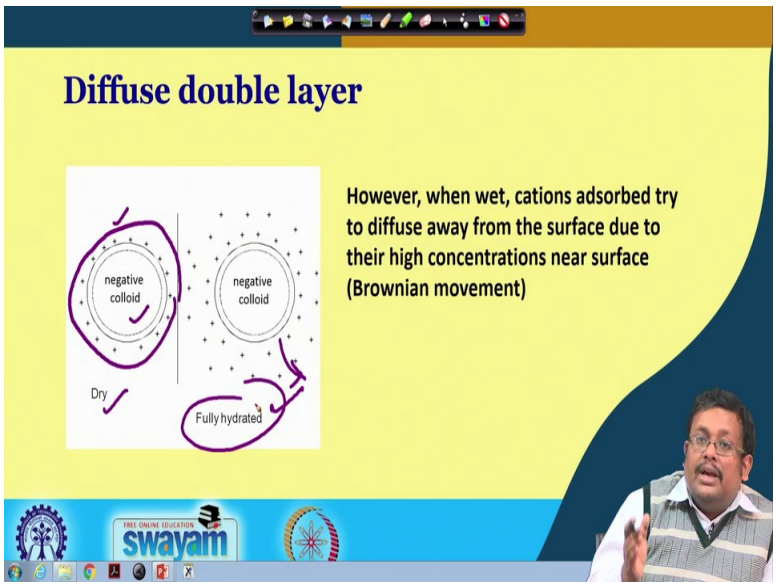

Now, diffuse double layer comes into question when the soil is wet. So, when wet cations are adsorbed or cations adsorbed try to defuse away from the surface due to their higher concentration high concentration near surface, that is caused due to the Brownian movement. Now, you can see here this is a negative colloid and this is a this is in case of dry condition and this is fully hydrated condition.

So, in the dry condition you can see this negative colloid is surrounded by these you know positive charge cations which are tightly bound. However, when there is a fully hydrated condition obviously, these tightly bound cations will try to diffuse away due to their Brownian movement and that is the you know condition when diffuse double layer comes into action. So why, let us see.

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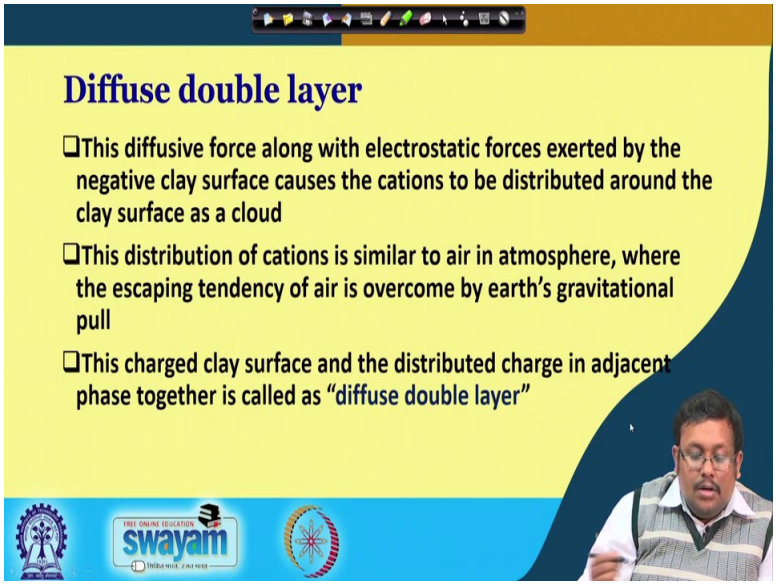

So, this diffusive force along with electrostatic forces exerted by the negative clay surface causes the cations to be distributed around the clay surface as a cloud. As you can see in the last slide also their surrounding the clay you know negatively charged clay colloid is a cloud like formation.

So, this distribution of cations is similar to air in atmosphere where the escaping tendency of air is overcome by earth's gravitational pull. So, there is a counter balance, I mean there is a balance between these two factors.

So, this charge clay surface and the distributed charge in adjacent phase together is called the diffuse double layer. You can see the charge clay surface and adjust and distributed charged in adjacent phase together is called diffuse double layer. The first layer is made by these negatively charged clay surface, the second layer is made by this distributed charges or ions.

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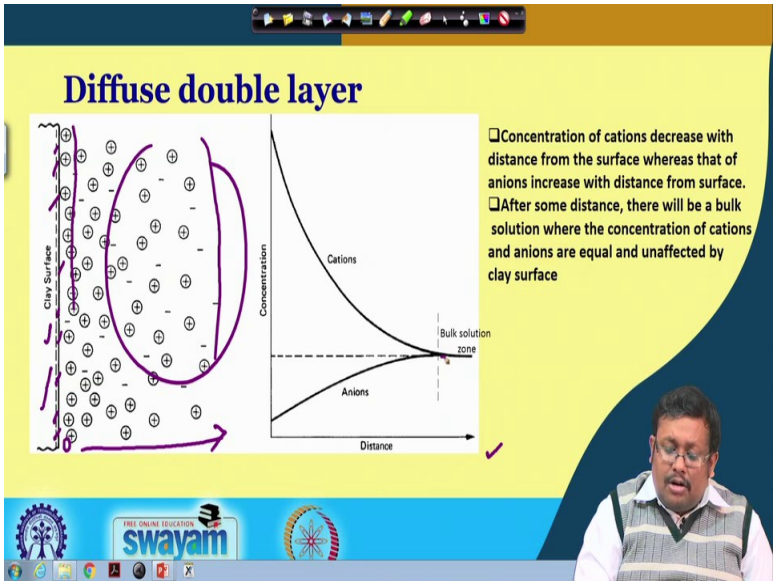

So, this is a diffuse double layer. You can see here if this is a clay surface; obviously, it will develop negative charge as you can see and this negative charge will be satisfied by this positively charged cations. However, if you see the distribution of the cations obviously, they will be highly concentrated along the surface of the clay. However, their concentration will decrease as they move away or you know go to the further distance from the clay surface.

So, basically they are diffusing. So, this graph also shows the relationship between the distance and concentration. So, as the distance increased both the cation concentration getting decreased and also and anion concentration is increasing, because obviously, when there will be negative charge at the clay surface there will not be high amount of anions because of repulsion. So, there will be minimum amount of anion present at the near vicinity of the clay surface. However, as he go further away from the clay surface there increase their concentration will be increasing as you can see in this picture their concentration is increasing in this zone. So, obliviously the anion concentration will

increase and the bulk solutions zone after a certain distance they will be present in equilibrium condition.

So, this is how the diffuse double layer looks like this will be. Firstly, clay surface you know this is the first layer followed by second layer of diffusing ions. So, the concentration of the cations decreases with distance from the surface where that is of anion increases with distance from the surface and after some distance there will be a bulk solution where the concentration of the cations and anions are equal and unaffected by the surface. So, after the certain distance you see there is there are almost similar. So, there is unaffected further from the clay surface. So, this is the diffuse double layer.

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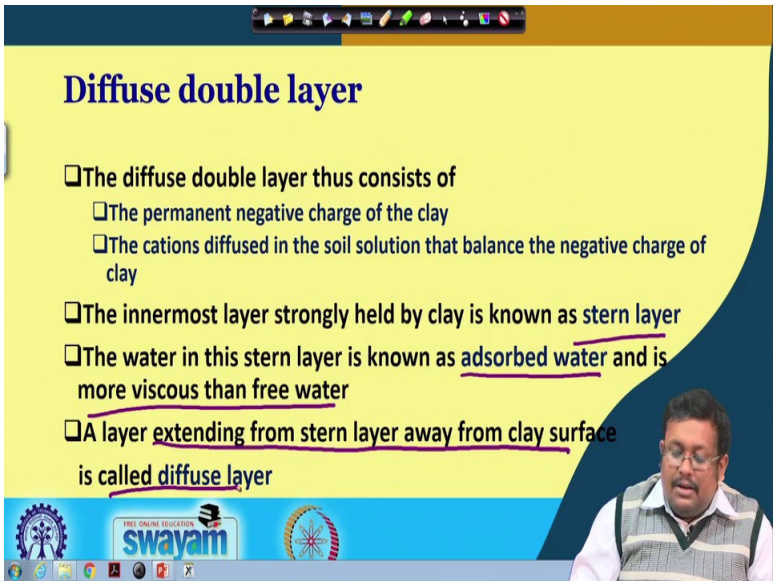

So, the diffuse double layer thus, consist of the permanent negative charge of the clay and the cations diffused in the soil solution that balances the negative charge of the clay. So, that is how a diffuse double layer is basically made of. So, innermost layer strongly held by the clay that is known as the Stern layer will discuss what is Stern you know in couple of minutes and the water in this Stern layer is known as the absorbed water and is more viscous than the free water. And, a layer extending from Stern layer away from clay surface is called the diffuse layer will see what are the Stern layer and diffuse layer.

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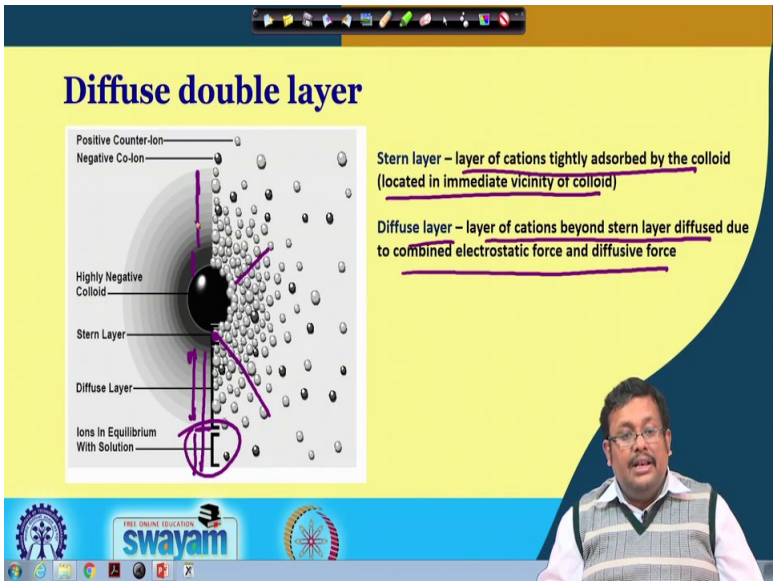

So, if we go so, this is the Stern you know this is the pictorial depiction of a diffused double layer. So, let us see this is the highly negative clay colloid here and it is first surrounded this negative charges for satisfied by the by the cations at the nearest vicinity creating the Stern layer. Here the Stern layer is basically here this black zone which is surrounding this highly negative colloid. And, as a result if you see as we move forward as a move ahead from this you know from the surface of the negative colloids the concentration of the cations is getting decreased and this zone is called the diffused layer. And obviously, after certain distance after the certain distance you will see the ions in equilibrium in the solutions. So, there will be both positive cations and negative anions.

So, the Stern layer is the layer of cations tightly adsorbed by the colloid located immediately vicinity of the colloid which is almost black in color in this picture as the diffuse layer is the layer of cations beyond Stern layer diffused due to combined electrostatic force and diffusive force. So, if you consider this is the Stern layer and this will be the diffused layer. I hope that now I hope that it is you know you can understand.

Now, obviously, at the equilibrium with the when the ions will be equilibrium solution you see both positive counter ion and negative counter ions, ok. The positive counter ions are this you know you know relatively you know this white circles whereas the black circles and negative colloids, ok.

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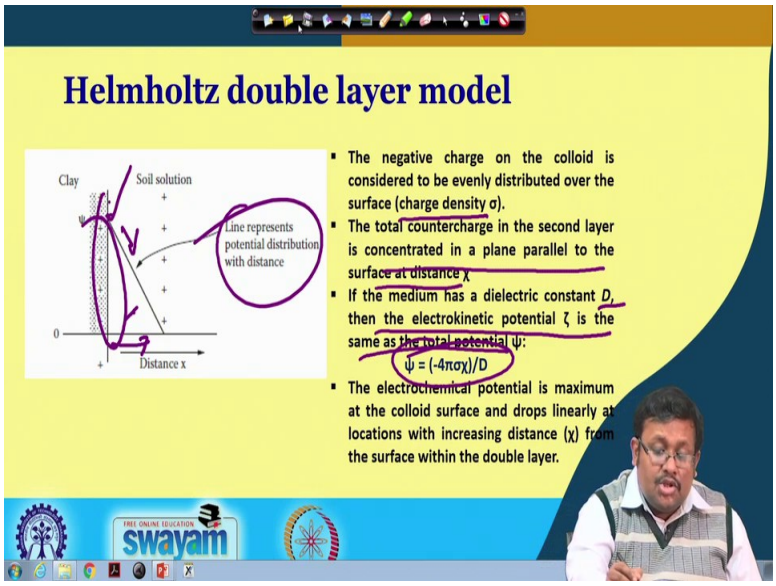

So, let us move ahead and see: what are the different models for expressing the diffuse double layer. So, the first model work is the Helmholtz double layer model which was given by the scientist Helmholtz is the first given double layer model. Now, in this model you can see the negative charge on the colloid is considered to be evenly distributed over the surface with the charge density of sigma and the total counter charge in the second layer is concentrated in a plane parallel to the surface at distance x.

So, if the medium has a dielectric constant D, then the electrokinetic potential zeta is the same as the total potential psi. And, we can calculate the total potential by using the formula. And, the electrochemical potential is maximum at the colloid surface here and; obviously, at it drops linearly as you can see it drops linearly at the location with increasing distance over here, when you are increasing distance it drops linearly.

So, obviously, you can see this line represent potential distribution with the distance and incase of Helmholtz double layer; obviously, there will be positive cations as you can see here the positive cations are congregated at the clay surface parallelly. So, obviously, this is the you know the total counter charge in the second layer is concentrated in a plane parallel to the surface and you know further as we move ahead will see that you know the potential is linearly decreasing. So, this is the Helmholtz layer.

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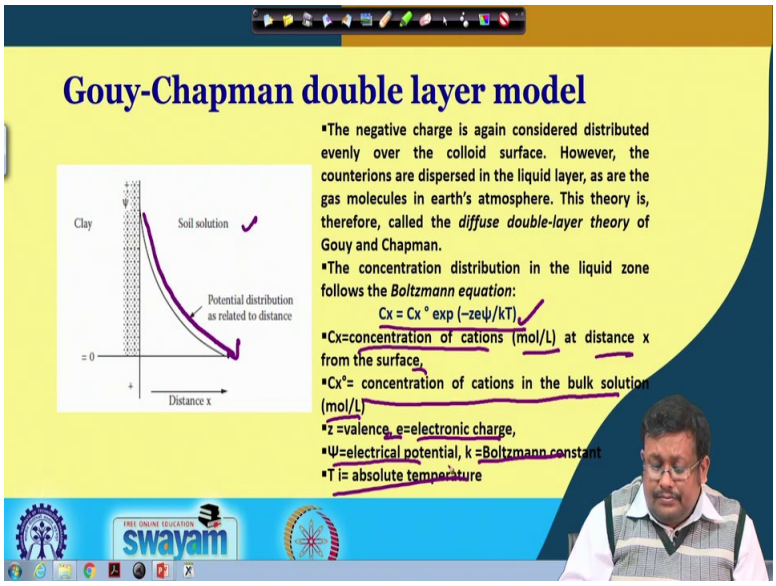

So, let us see what is the next layer. What is the further modification? Now, the further modification is Gouy-Chapman double layer model now the negative charge is again considered distributed evenly over the colloid surface; however, the counter ions are dispersed into the liquid layer as are the gas molecules in earth's atmosphere and this theory is therefore, called the diffuse double layer theory of Gouy and Chapman. So, you can see here this is the bulks we know this is soil solution and this is the distance x from the clay surface the potential distribution you can see there is a I mean there is a exponential decay in the potential as we go from the clay surface.

So, the concentration distribution in the liquid zone follows the Boltzmann equation and the Boltzmann equation can be denoted by this equation. So, C x is basically concentration of the cations in mol per liter at distance x from the surface and C x^0 is basically concentration of the cations in the bulk solution mol per liter and z is valence and e is electro electronic charge, psi is electrical potential, k is the Boltzmann constant and Ti is the absolute temperature. So, we know we have seen: what is this Gouy-Chapman double layer model.

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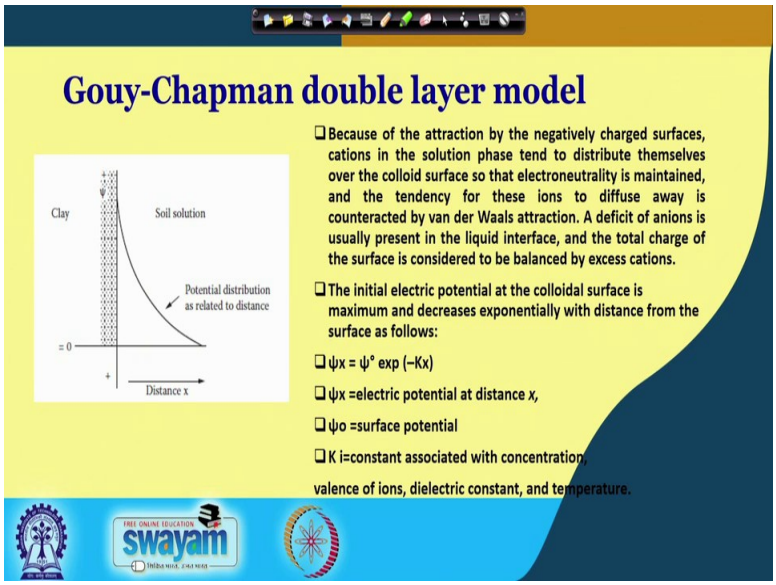

Now, because of the attraction by the negatively charged surface cations in the solution phase tend to distribute themselves over the colloid surface, so that electro neutrality is maintained. Obviously, when their will be negative charge it will be you know this you know the cations will try to distribute themselves over the surface to maintain the electro neutrality. And, and the tendency for these ions to diffuse away is counteracted by van der Waals attraction.

Obviously, when there will be congregation of cations; obviously, there will be charge of you know mutual repulsion and mutual repulsion will also be counter balanced by the van der Waals attraction force. A deficit of anions is usually present in the liquid interface and the total charge of the surface is considered to be balanced by excess cations, we know all these things. So, the initial electrical potential at the colloid surface is maximum and decreases exponentially with the distance from the surface as follows we know all these things.

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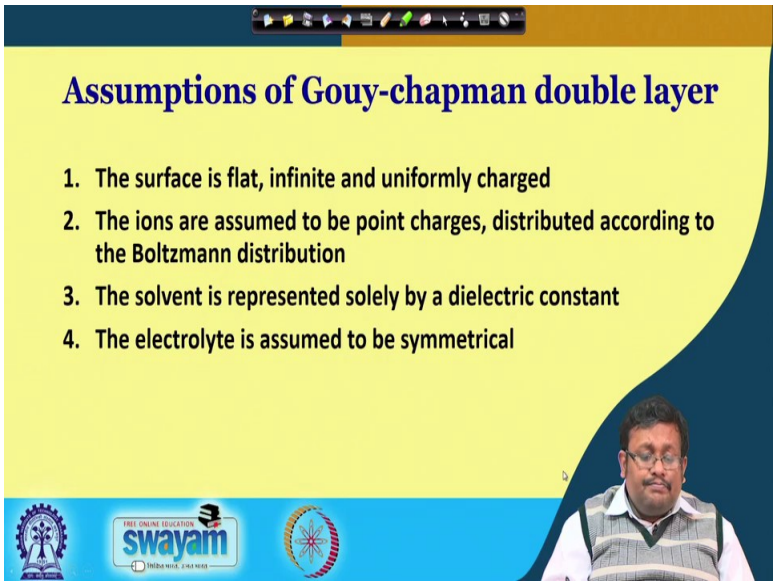

So, you know let us go ahead and see what are the assumptions of Gouy-Chapman double layer. There are four major assumptions of Gouy-Chapman double layer the surface first of all the surface is flat and infinite and uniformly charged. Second the ions are assumed to be point charge distributed according to the Boltzmann distribution; thirdly this solvent is represented solely by dielectric constant and electrolyte is assumed to be symmetrical.

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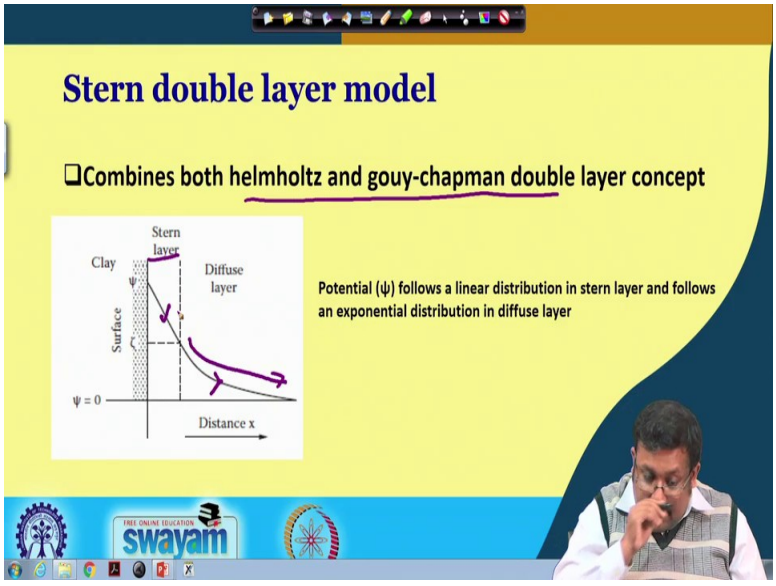

Now, all this both Helmholtz and Gouy-Chapman they try to describe these adsorption you know they try to describe this diffuse double layer or double layer the distribution of the counter ions in the in the in the soil and liquid interface. However, both of them has some you know have some limitation. So, Stern gave another model which we call Stern double layer model. Now, Stern double layer model basically it combines both Helmholtz and Gouy-Chapman double layer concept. So, how so, you know according to Stern you know potential follows a linear distribution in Stern layer. So, this is called the Stern layer. In the Stern layer obviously, there will be you know the counter ions or cations will be tightly adsorbed over the clay surface.

However, away from the Stern layer there will be a diffuse layer where the further cations will diffuse away with the increase in the distance. So, this is how we call a Stern double layer model. So, you can see there will be both linear and exponential decay of the potential from the clay surface. So, if you remember in case of Helmholtz they say there is a linear decrease of potential as we increase the distance from the clay surface and in case of Gouy-Chapman there is a you know exponential decay of potential from the clay surface and these basically a synthesis of both of these. So, you can see a combination of both linear as well as you know exponential decrease of the exponential decrease of potential. So, this is how it is called Stern double layer model.

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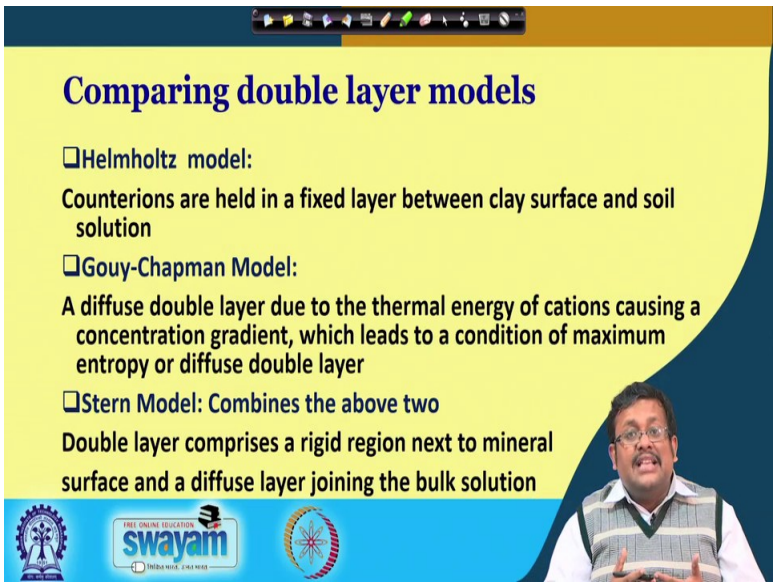

So, comparing how is the let us compare this three models. Helmholtz model, obviously, counter ions are held by a fixed layer between clay surface and soil solution and Gouy-Chapman model – a diffuse double layered due to the thermal energy of cations causing a concentration gradient which leads to a condition of maximum entropy or diffuse double layer; you know entropy means the degree of randomness. So, maximum entropy is maximum randomness and as a result they will diffuse away.

Stern model basically it combines the above two model and double layer comprises of a rigidness rigid region next to the mirror surface and a diffuse layer joining the bulk solution. So, this is how this Stern model combine both this model.

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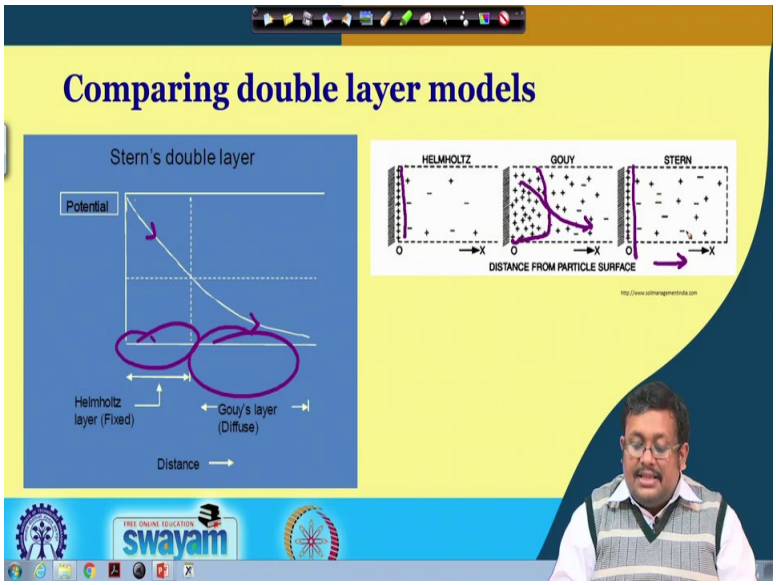

So, again this also shows a very good representation. So, this is Stern model you I have already discussed there is a linear and exponential decay of potential. So, the first one is basically Helmholtz, the second one is Gouy's layer. So, this is basically synthesis of these two model.

So, another here you can see in the Helmholtz the counter ions are you know are you know adsorbed parallel in the parallel plane just in the vicinity of the clay surface. However, in the Gouy you can see you know the most of the cations are concentrated; however, there is a you know exponential decay of concentration of the cations as we increase the distance and in case of Stern they are two types of layers: one is the fixed potassium layer here and there is a further diffuse you know of not potassium layer and

the cation layer adjacent to the clay surface and this cations will further diffuse away as we increase in the distance. So, distance from the particle surface in the x-axis. So, this is basically how we can visually you know if you visually compared this double layer models we can see these differences, alright.

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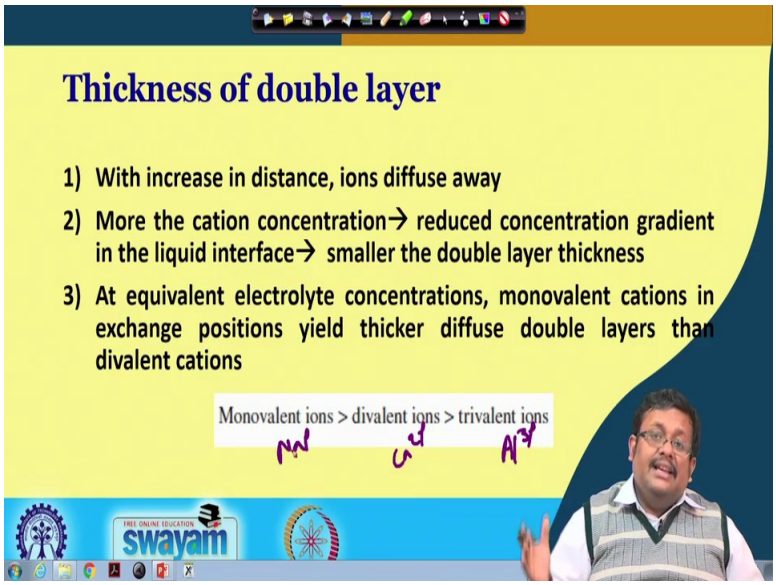

So, now this is very important concept. You see there are thickness of the double layer it is it is variable. How do you know: what is the thickness of the double layer and how it varies? Now, thickness of the double layer is dependent on several factors first of all with the increase in the distance ions diffuse away because when there will be increase in the distance from the clay surface, obviously, they will try to defuse away because their attractive force will decrease and as a result they will further diffuse away to the bulk solution. And, more the cationic concentration if you add more cationic concentration it will reduce the concentration gradient in the liquid interface and as a result of the reduced the reduction of the concentration gradient in the liquid interface you know it will make the double layer thickness reduce .

So, it will reduce the double layer thickness. Obviously, because how because when we increase the cations concentration it will try to congregate all the cations at the clay surface and as a result of their communication at the clay surface; obviously, we know the tendency of cations to defuse away will reduce an ultimately it will reduce the

concentration gradient in the liquid interface and ultimately it will make the you know the thickness of the layers smaller.

And, at equivalent electrolyte concentration, monovalent cations in exchange positions yield thicker diffuse double layer than divalent cations. So, if the cation is sodium it will produce thicker you know diffuse double layer than that of a divalent cations like calcium, than that of a trivalent cations like aluminum. So, obviously, it depends on the valency of the cation; obviously, when there will be sodium present the that thickness of the diffuse double layer will be highest followed by calcium and then so on so forth.

So, obviously, based on the electrolyte concentration when we increase the electrolyte concentration and when we increase the valency of the cations which are present in the electrolyte, obviously, the thickness of the diffuse double layer will decrease.

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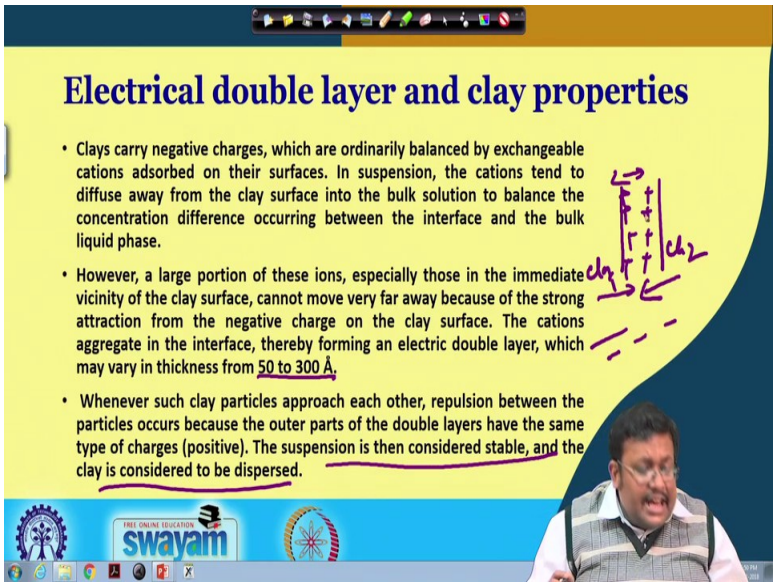

So, what is the implication of this thickness of the diffuse double layer? This is very important, that is why we are learning this diffuse double layer and its theories. Now, you know that clay carries a negative charge and which are ordinary balanced by exchangeable cations adsorbed on their surface and in suspension the cations tend to diffuse away from the clay surface into the bulk solution to balance the counter the concentration difference occurring between the interface in the bulk liquid phase, it is the natural phenomena. However, a large portion of these cations especially those in the immediate vicinity of the clay surface cannot move very far away because of the strong

extraction from the negative charge on the clay surface. And, the cations aggregating to the interface there by forming electrical double layer. We have known all these things so far which can vary in thickness from 50 to 300 angstrom. So, you can see it is the large range.

Now, whenever such clay particles approach together for example, let us see this clay particle with high congregation of the cations this is another clay particles with communication of cations. So, when this two clay particle clay 1 for example, clay 2 they will you know they will they will move you know they will approach to each other. Obviously, there will be repulsion between these positive charges.

So, as a result of this repulsion between the outer parts of the double layer have the same type of charge. So, the suspension is this considered stable because as a result of repulsion they will not come close together, they will not form a aggregate. As a result they will be dispersed into the soil into the soil solution. As a result of the dispersion to the soil solution there is this will be you know then it will be called a stable suspension. And, the suspension is this constable and the place considered to be dispersed.

Again, due to the you know due to the presence of positive charge cations in the clay particles. When the clay particles will come close together there will be repulsion. As a result of repulsion they will not from the you know they will not form aggregate as the result of non-formation of aggregates they will remain to the solution in dispersed condition; as a result the suspension is considered stable and you know there will be no flocculation.

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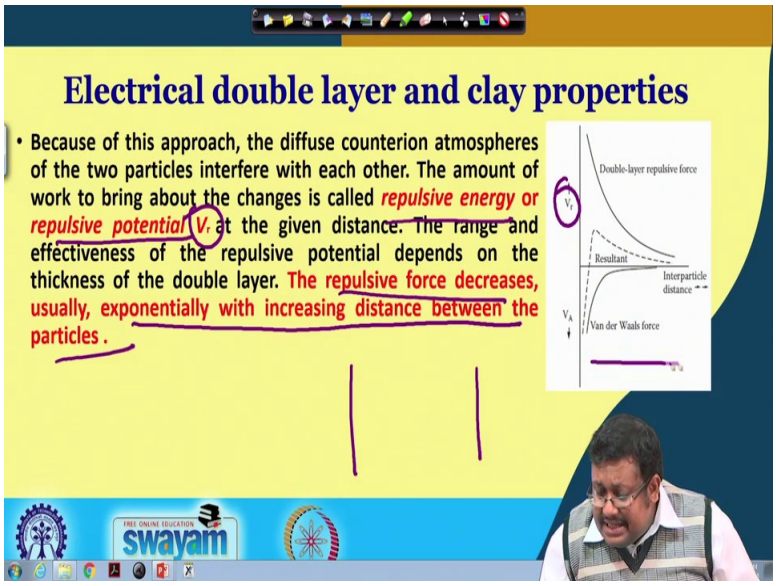

Now, because of this approach because of this approach the diffuse counter ion atmosphere of the two particles interfere with each other and amount of work to bring about the changes is called repulsive energy repulsive potential which is denoted by V r; Vr at the given distance. Now, the range and effectiveness of the repulsive potential depends on the thickness of the diffuse double layer and the repulsive force decreases. Obviously, at you know usually exponentially with increasing distance between the particles because when the particles will be the further away the repulsion will be decreased. So, you can see here the repulsive force which is denoted by Vr is decreasing continuously with the increase of the distance inter-particle distance.

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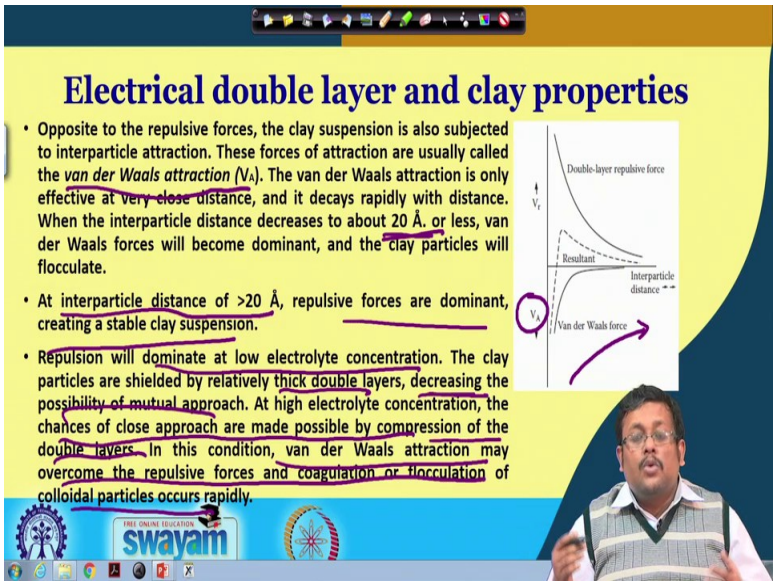

So, this is clear. So, let us see what are the other implications. Opposite to the repulsive force the clay suspension is also subjected to interparticle attraction. So, there are two forces: one is repulsive forces and another is attractive forces and these forces of attraction are usually called the van der Waals attraction or Va; this is van der Waals attraction force. Now, the van der Waals attraction is only effective at very close distance and it decays rapidly with distance as you can see it decays rapidly with distance and when the interparticle distance decreases to 20 Armstrong or less van der Waals force will become dominant and the clay particle will flocculate.

Now, as a result of this van der Waal attraction when the interparticle distance is less than 20 Armstrong; obviously, these two particle will further club together and it will it will flocculate. And, at the interparticle distance of greater 20 Armstrong repulsive forces are dominant creating a stable clay suspension. So, again it all depends upon the interparticle distance.

When the interparticle distance is greater than 20 Armstrong the repulsive forces will be dominant. As a result of the repulsive forces there will be repulsion between the two particle because of the similar positive cations in the outer surface and as a result the state the condition will be stable; that means, that with the soil will be dispersed, there will be no flocculation. However, when the interparticle distance comes goes down below 5 Armstrong there will be van der Waal attraction, as a result of the van der Waal

attraction the resultant you know as a result of the van der Waal attraction these particle will you know will club together and create the flocculation.

So, repulsion will dominate at low electrolyte concentration obviously, because at low electrolyte concentration the thickness of the diffuse double layer is greater. The clay particles are shielded by relatively thick double layers in case of low electrolyte concentration decreasing the possibility of mutual approach. So, if there is no mutual approach, obviously, there will be you know there will be you know no attraction. So, I mean the repulsion will dominate low electrolyte concentration because the decreasing the possibility of the mutual approach. Mutual approach will be very less for mutual approach you need interparticle distance less than 5 Armstrong as we have already know. So, I am sorry 20 Armstrong 20 Armstrong.

So, when it is less than 20 Armstrong van der Waal attractive force will be dominant. However, when the repulsive will be dominated low electrolyte concentration and the clay particles will be shielded by relatively thick double layers and decreasing the possibilities of mutual approach and at high electrolyte concentration the chances of close approach are made possible by compression of the double layers. We know that when we increase the more electrolyte concentration the thickness of the double diffuse double layer will decrease and as a result will be there will be further compression and you know in this condition van der Waal attractive force may overcome the repulsive force and coagulation and flocculation particles occurs rapidly.

So, resultant force will be more and as a result there will be flocculation or coagulation. So, which one is better? The question is which one is better? Well, for well aggregation obviously, it is better to have a well aggregate I mean for better plant growth and better soil physical and chemical properties you need to have a better aggregated soil. So, you must encourage soil flocculation and coagulation for better aggregation. If the soil is dispersed this is not good for soil physical as well as biological activities and chemical activities. We will discuss that later on.

Now, another important aspect let us see. So, in a nutshell you see that when the interparticle distance are higher; obviously, repulsive forces will be dominant were more than 20 Armstrong and when the you know when the interparticle distance is less than 20 Armstrong attractive forces you know van der Waal forces will be dominant and all this

depends on the thickness of the double layer and thickness of the double layer you know can be changed by increasing the concentration of the electrolytes and you know and also you know the changing the valency of the cations which are present in the electrolytes.

So, let us stop here and in the next lecture will be covering zeta potential and then will go to our next topic that is adsorption isotherms.

Thank you very much.