Novel Separation Processes
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Lecture No. # 37
Chromatographic Separation Processes (Contd.)

We will look into the let say principle walk in principle of in a chromatographic column; and we are looking in to the solute movement theory. From this, from conducting the under time theory, we will be able to predict at exactly part retention time and the subject to the column characteristic on the property of the solute. The at whatever retention time the solute at the particular solute will be appearing in the outlet of the chromatographic column, so that the separation will be prominent and there will be able to trap the separation.

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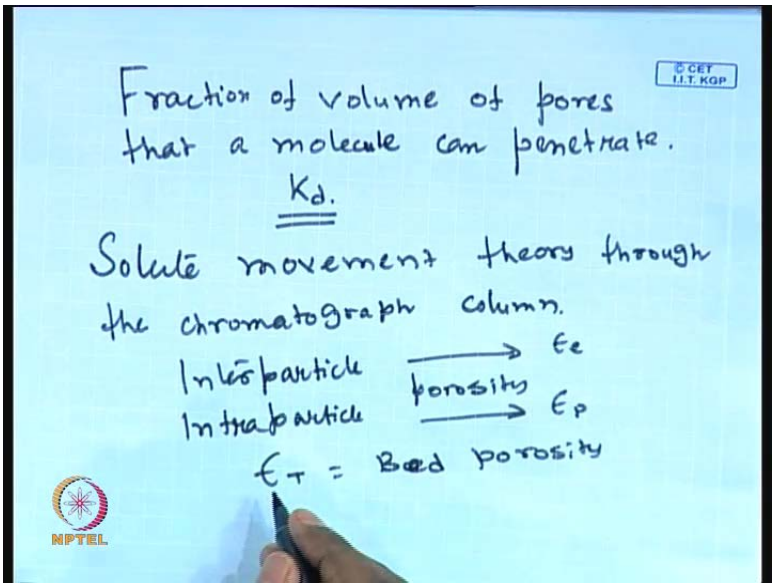

So, we are looking in to the principle of the solute movement theory through the column. The first definition we had you defined various in porosity of the inter particle and intra particle porosity. This defined as the epsilon e this is defined as the epsilon p in a talked about the bed porosity, total bed porosity. Then we will be talked about the various types of you know densities, bed densities, particle density and fluid density, the crystalline bed density so and so forth.

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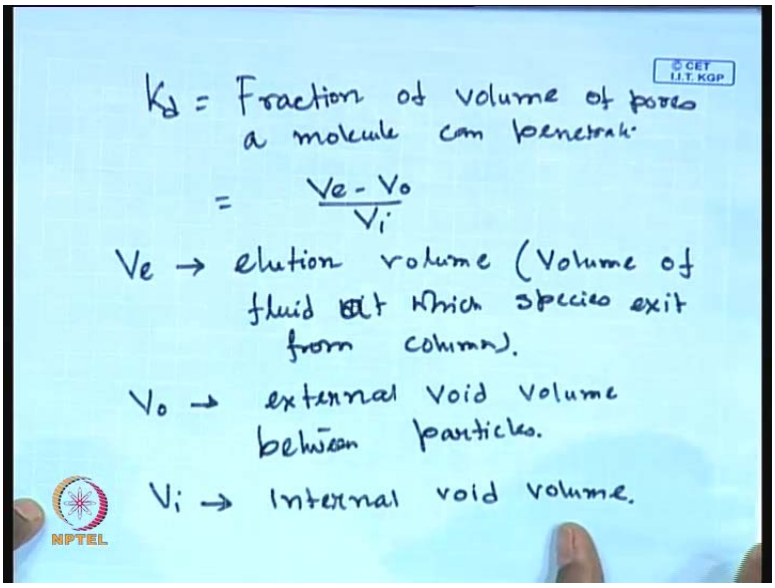

Next, we defined a quantity call K d, K d is nothing but the fraction of volume of pores that a molecule can penetrate. This is defined as V e minus V naught divided by V i, we defined different volumes. V e is nothing but the elution volume, volume of flute at was the species exit from the column.

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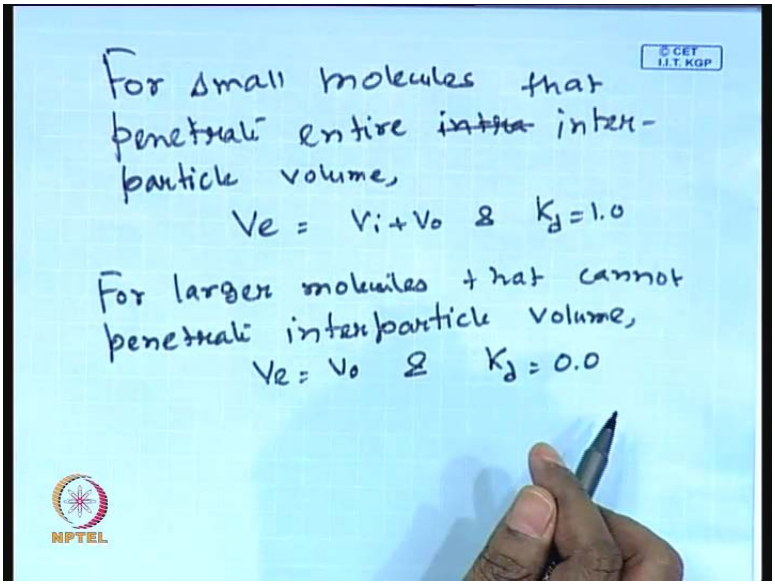

This volume is nothing the volume of fluid at which species exit from the column. What is V naught? V naught is external void volume between the particles and V i is internal void volume. Now, for small molecules that can penetrate the entire inter particle

volume, inter particle for small molecules with can penetrate the inter particle volume the value of K d is 1. Molecule that penetrates entire intra particle volume, inter particle, sorry, volume V e is equal to V i plus V naught and K d is equal to 1 in the particular case. For larger molecules, that cannot penetrate inter particle volume because of size exclusion V e will be is equal to V naught and in that case K d will be is equal to 0.

So, for larger particle K d will be assuming the volume of the 0 where which you cannot know penetrate to the inter particles space and it will be excluded because of the higher larger size. And for smaller particles give the value of K d will be equal to 1. Now, let us once we have this types of definition, basic definition let us look in to the what are the processes involved in a typical chromatographic column.

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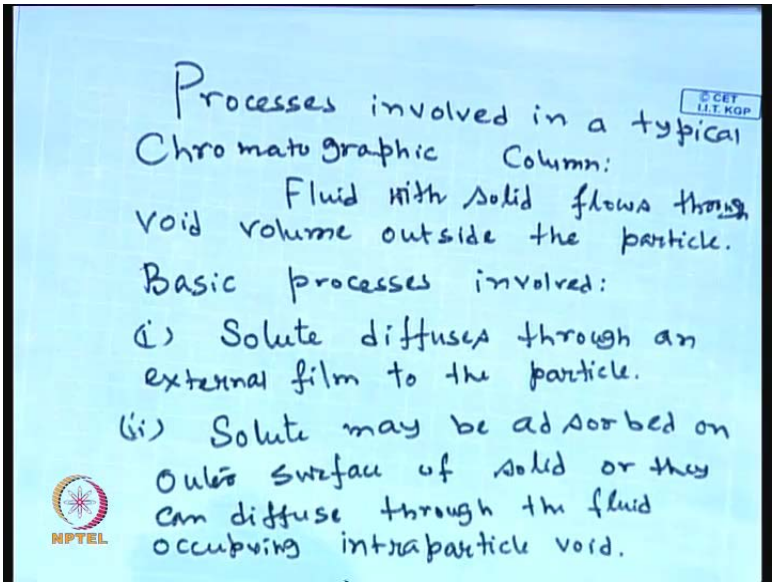

So, let us look in the processes is involved in a typical chromatographic column. Now, fluid containing the solid forces in the void volume out side the particle. Fluid with solid flows through void volume out side the particle. Now, the basic processes there are involved in to this transport at given below; number one is that solute diffuses through an external film to the particle. Diffusion of solute, solute diffuses through an external film to the particle solute absorb on solute can get absorb and external surface or diffuse through the turbulent fluid in to the force. Solute there may be solute absorption on the outer surface of the particle are fluid may be going in to the in a pores of the of a particle itself because the particle is porous.

The solute may be absorbed on outer surface of solid as well as or they can diffuse through the fluid occupying intra particle void. Now, if the pores are ex so, they may be have the going physically absorbed on the other outer surface or they may be going there the in a particle, the particle is itself is porous the pores are filled with the liquid are the fluid and the solute may be diffuse through it is liquid inside the in to pores inside the particle.

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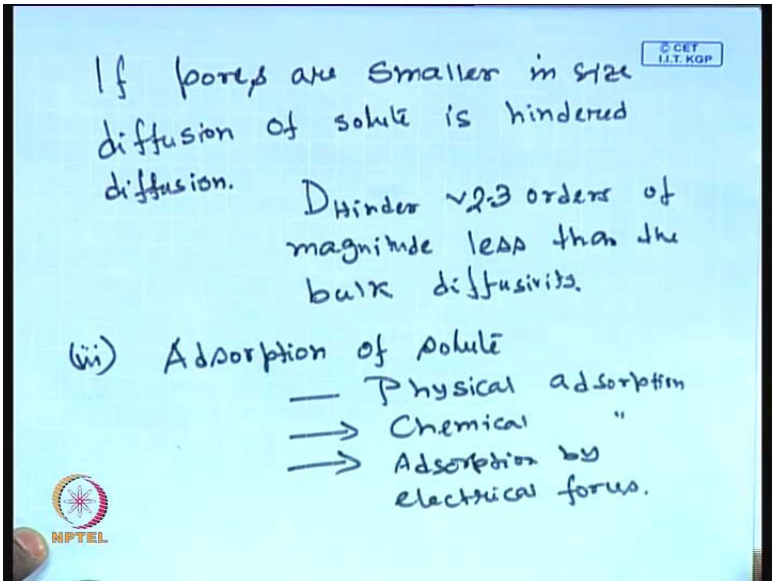

If the put the pores are small, this diffusion will be a in the diffusion. Pores are smaller in size, diffusion of solute is hindered diffusion. And typically the coefficient of hindered diffusion; that means, diffusivity hindered diffusivity will be 2-3 orders of magnitude less on the bulk diffusivity. So, D hinder is the around 3, 2 - 3 orders of magnitude less then the bulk diffusivity. So, third feature is third process that is involved is solute points a back and side and then observed by physical or electrical pores are chemical reactions. The adsorption of solute may be involve the three adsorption solute may be physical adsorption, it can be a chemical adsorption, it can be adsorption by electrical forces. That means, if you have a ionic nature; that means, there is a suppose the solute is (( )) and the will be having ion, it and the will be having ionic sides on the adsorption, there may be electrostatic attraction or electro static attach of the solute for the solute matrix.

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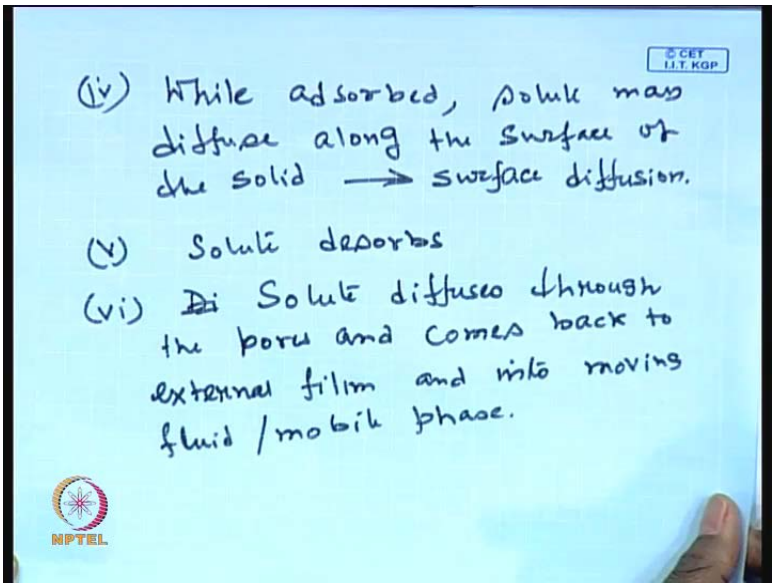

So, fourth process will be void at void absorbed solute may diffuse along the surface of the solid. This is known as surface diffusion. The another process surface diffusion may take place on the surface itself. That means, the solute is absorb on a particular position of the solute particles, then a diffuses along surface. That means, it what does; that means, the previous side as become vacant that side will be available for a adsorption another solid solute so that solute will be absorb then we again can moves along the surface by diffusion and then another solute can be absorbed over it. Now, the last one is, even after adsorption solute desorbs to some extend and there will be equilibrium of adsorption, desorption cycle. It is like any normal adsorption type of process. Next, the diffuses that means, solute diffuses to the pores and comes back to external film and into moving fluid or mobile phase.

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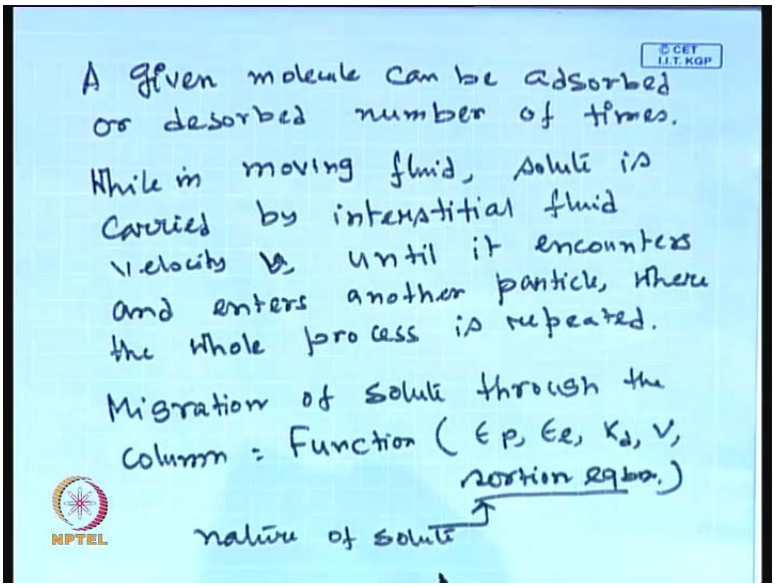

That means, after desorption it diffuses through the pores it comes back to the ex through the external film and a again go goes in to the mobile phase. Now, a given molecule can absorb and desorbs a number of times. So, there is not the it will be one time of a given molecule can be adsorbed or desorbed number of times while in moving fluid. That means, in the mobile phase the solute is carried along the interstitial fluid velocity V, solute is carried by interstitial fluid velocity V, until it diffuses another particle and where whole process is repeated. Until it encounters and enters another particle where the whole process is repeated; that means, again it will be the adsorbed. It may be adsorbed in to the pore get it is may be surface diffusion.

It may be again desorbed, it may be diffuse (( )) fluid in the pore, it will come to the external film and then it will be desorbed again the moving phase. So, it can be the same solve solute particle can encounter into the different particles and can get into it and then come back so that whole process will be delight. So, when it will be coming out there will be a finite residence time, it will not be instantaneous this means what this basically you are abstracting the so, it in that things whole process is basically you are abstracting the path of a solute particle in by the by imposing the column.

So, in a sense the mobile phase that will be the coming out of the column, it will not be having instantaneously the value of the solute present of the solute there. The present of the solute will be delight; that means, the finite residence time for particular solutes. And

the hindrance to the solute particles offered by the fluid will be different for the solutes because depends on the solute characteristic as well as. That means, solute A can be absorbs more easily by the column material. So, the solute be will be coming faster in the in the outer phase, in the elegant phase. And if and so, therefore, will be a finite difference of residence between the solute B and solute A. So, it can easily separate them out, that is the idea.

So, let us talk about and this migration of the solute is obviously, a function of several thing migration of solute through the bed or through the column is a function of epsilon p epsilon e K d v that is the solute interstitial velocity. And of course, the sorption equilibrium, this sorption equilibrium is nothing but the absorption equilibrium. That means, this absorption equilibrium will be different for a different types of solutes. So, of course, when you put this it simply means this migration of solute through the column will be function of nature of the solute as well. So, absorption equilibrium will be in a function of nature of the solute. That means, same solute cannot be absorb in the same manner of the another solute of the same absorbent, there will be different in nature. That will be typically dictated by the absorption equilibrium. Now, let us looking to a schematic diagram of a get the differential column.

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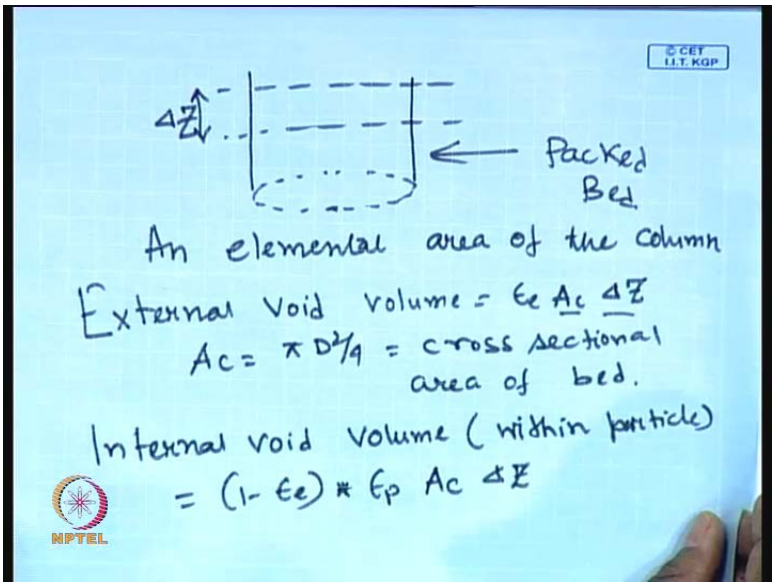

So, let us this suppose this is a packed bed, this is a cylindrical column, the packed bed and the talking about a cross section of height delta Z. So, this is an elemental area of the

column. Now, external what is the external void volume? External void volume is given as epsilon e multiplied by A c time delta Z. Epsilon is the volute fraction a void fraction. So, epsilon e multiplied by A c into delta Z is the differential volume of differential element. E e A c is the area cross section delta Z is the height this gives the volume, differential volume of the element that talking about with in the high delta Z. That should be multiplied by the epsilon e that will give you the external void volume. So, A c is nothing but pie D square by 4 are cross section area, area of bed.

An internal void volume let us look into that. Internal volume, void volume within the particle, this given as 1 minus epsilon e is the other void fraction multiplied by epsilon p because epsilon p is the void volume of the inside the particle multiplied by A c times delta Z. Now, solute in the bed it can be in the mobile phase or in the external volume or it can be stagnant liquid phase inside the particle or it can be sorbs on the particle.

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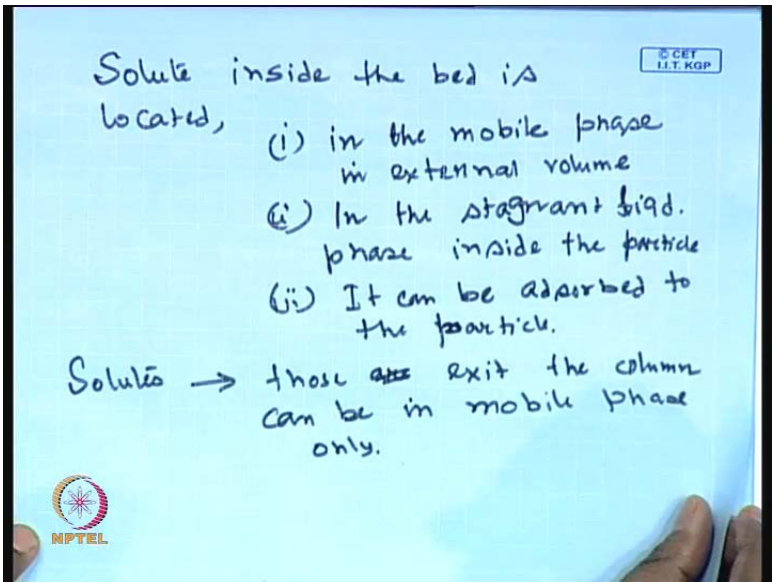

So, there may be three types of location of where is you can find a solute inside the bed. So, solute inside the bed is located either anyone of this or all of them or some two of them. First one it will be in the mobile phase in external volume secondly, it can be in the stagnant in the liquid phase inside the particle or it can be solved to the particle absorbed to the particle itself. The solutes those are outside or those exit the column, they can be only in the mobile phase only. That means, we are not allowing bleeding of any solute particles from the column. So, any solid particle for the absorbent column will be

kept intact with in the column itself, none of them will be coming out or it is blood out from it.

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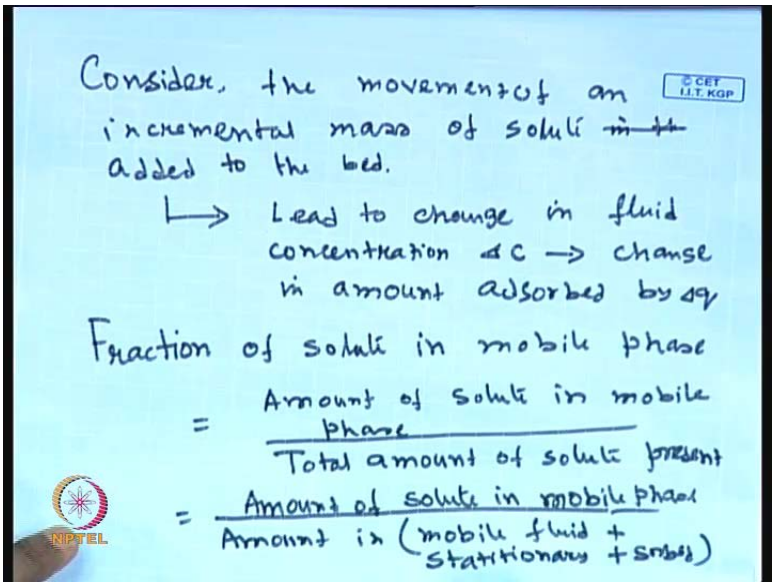

Now, let us considered the movement of an incremental mass of solute added to the bed; let us considered the movement of an incremental mass, incremental mass means the mass of the solute that is present will be in that differential element you have to just considered and incremental mass of solute added to the bed. So, what it will lead? It will change, it will lead to change in fluid concentration delta c and that will lead to change in amount absorbed by delta cube.

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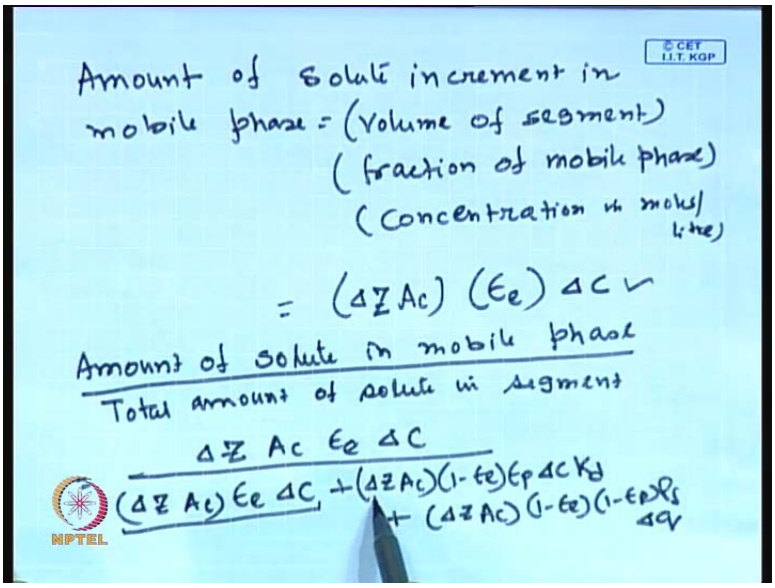

So, fraction of solute in the mobile phase, is what? Mobile phase is given as amount of solute in mobile phase divided by total hour total amount of solute present in the segment solute present. So, this is nothing but amount of solute in mobile phase divided by the amount of solute in mobile phase, last stationary phase, last amount absorb. So, there are three location we say they can be present. The solute may be within the column it may be present in the mobile phase, it can be present in the stationary phase, with in the solute and it can be in the form of adsorb part on the solute surface itself.

So, in the denominator, the amount of solute must be in mobile phase, mobile fluid plus stationary fluid plus amount sorbs or absorb on the solute particles. Now, amount of solute increment in mobile phase because of the delta c, solute increment in mobile phase it will be how much? It will be volume of the segment. I am talking about the elemental of volume of that discussed volume of segment or elemental volume multiplied by the fraction which is mobile fluid, fraction of mobile phase concentration in moles per litre, multiplied by the concentration moles per litre.

So, volume of the segment will be delta Z multiplied by area cross section plus segment. Fractions of the mobile phase will nothing but epsilon e. And what is the concentration in moles per litre? That is the delta c. There is the solute amount solute increment in mobile phase. So, amount in mobile phase about amount of solute in mobile phase, mobile phase divided by the total amount of solute in the segment will be what? The

amount of solute in mobile phase will be given by this quantity. So, this value in the demonic in the numerator delta Z A c epsilon e times delta c.

And the total amount of solute present in the segment; that means, in the column itself, it will be having in three locations. One is the mobile phase and is the stationary phase with in the pore and another is the adsorb in the form of adsorbed phase on the solute. So, the first one will be delta Z A c times epsilon e times delta c that is the amount present on the mobile phase plus delta Z A c is the volume multiplied by 1 minus epsilon e times epsilon p delta c times K d and delta plus delta Z times A c multiplied by 1 minus epsilon e multiplied by 1 minus epsilon p times rho s times delta q.

So, this amount will be is present in the mobile phase. This amount of solute is present in the within the pore of the particle. Delta Z times A c is a cross section is the elemental volume multiplied by 1 minus epsilon e. 1 minus epsilon e is the void volume that is present will be in the particle. And within the particle the void fraction is epsilon p. So, it should be multiplied by epsilon p, multiplied by the delta C, but it entirely depends by the K d typical to 1 and not or K d is 1 or 0 that means, K d is what? The K d is the amount of the solute that will be at all moving in to the force or not by the size exclusion if it is larger, it will be is equal to 0.

So, there is no question of the solute present with in the pore. If K d is the assuming some value some amount of solute will be moving in to the pore so, you should multiplied by the fraction K d. So, this amount is the amount present in the mobile phase this term will indicate the amount present in the solid phase. And what is the amount? This amount this one minus epsilon e; that means, the porous that is the porous particle volume power fraction of the porous particle multiplied by 1 minus epsilon p.

That means, the will in the pore the will in the particle the pores are present 1 minus epsilon p is that volume fraction where the solid materials present. So, 1 minus epsilon e into 1 minus epsilon p is the overall compare to the overall bed, what is the solid material is present on that it will be absorb. Delta q will be amount that will be observed have a (()) and rho is the density of the solute particles. So, this is the third term presents are it represent the amount of solute that will be absorb on the solute particle.

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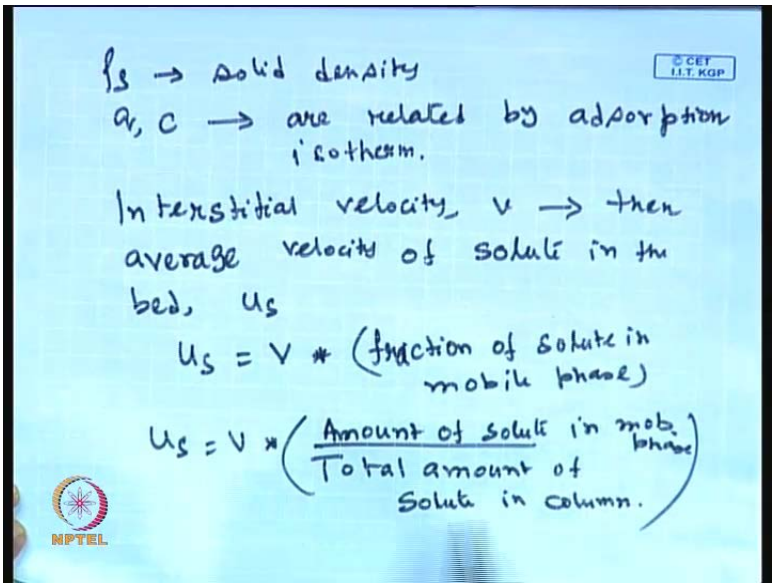

So, what is rho s? Rho s is nothing but the solute density. And what is q? q and c are related to the adsorption isotherm equilibrium. Now, you in a position to calculate the interstitial feed velocity or average velocity. So, if you have interstitial velocity V, then the average velocity of the solute in the bed is u s. And what is u s? u s is nothing but V multiplied by fraction of solute in mobile phase. And what is the fraction of solution in mobile phase? That we have already founded there is the amount of solute in the mobile phase, mobile phase divided by total amount of solute in the column. So, we can and you already had this expression the total fraction of solute present in the mobile phase and just put the expression.

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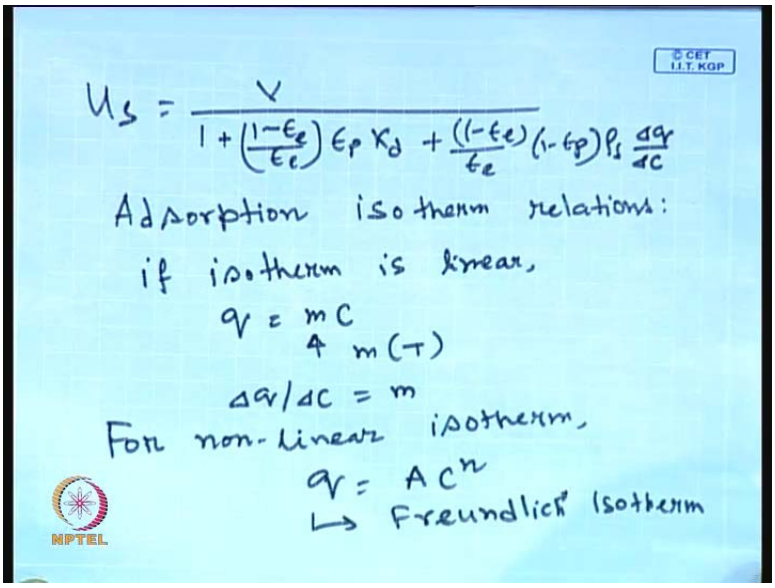

So, u s is nothing but V divided by 1 plus 1 minus epsilon e divided by epsilon e epsilon p K d plus 1 minus epsilon e divide by epsilon e 1 minus epsilon p rho s delta q by delta c. So, basically the expression that we have written earlier and going to put this expression this is the fraction of solute present in the mobile phase. So, that the amount present in the mobile phase divided by total amount present in the column so, I just divided by delta Z A c epsilon e and delta c in the numerator as well as the denominator. So, this will be cancel from the first terms will be getting the rest three terms in the denominator, but it after division.

So, u s is the velocity if now let us looking in to the adsorption isotherm relations. If isotherm is linear, q is equal to m times c where, m is the isotherm constant and m will be typically a function of temperature. So, delta q by delta c will be a constant m. So, it basically d q d c. Delta q delta c will be nothing but m. If isotherm is non-linear, for non-linear isotherm, let us a q is equal to A c to the power n, what is the isotherm called is a Freundlich isotherm If you remember there are several adsorption isotherm language (()) Freundlich so and so forth.

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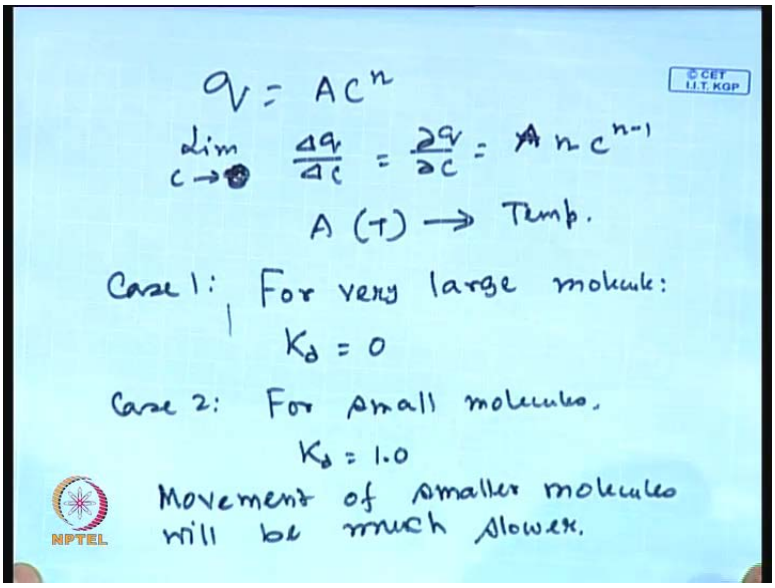

For a non-linear isotherm q is equal to A c to the power n limit c tends to infinitive delta q delta c tends to 0 delta q delta c will be nothing but del q del c and this will be A which may be a function of temperature, n c to the power n minus 1. So, this parameter can be A function of temperature as well. Now, case 1 for very large molecule so, delta q delta c can be can be written as a derivative with respect to c of the q expression. Because you know the q expression as function of c from the isotherm expression and you can derive take the derivatives of with respect to c and can get an another expression in terms of concentration.

For very dilute for very large molecule, K d will be equal to 0, K d itself will be equal to 0. And case 2 is for small molecule; that means, the second term will be present in the earlier expression in the denominator. For small molecules K d will be equal to 1. So, smaller molecules move slower because they will be moving into the pore of the absorbent particles. So much of them will be absorbed so, the amount that is present in the mobile phase will be less than less. So, whenever the mobile phase coming out the column the amount will be dilute initially then some amount of the things they desorbs then they will coming the mobile phase. So, the membrane smaller molecule membrane of that smaller particles or smaller molecules will be much slower.

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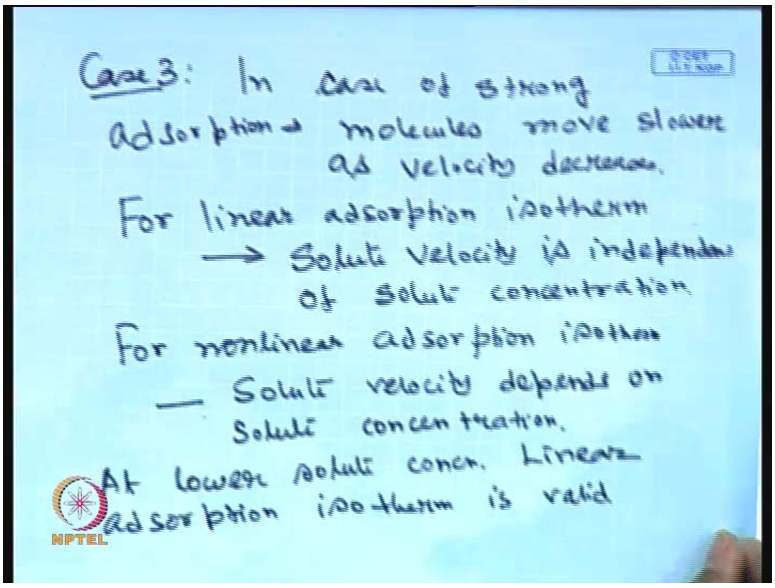

Now, next is next considered third case in case of strong absorption, molecules move slower as velocity decreases. In case of linear for linear adsorption, solute velocity does not depend on the solute concentration. Velocity is independent of solute concentration, why it independent? Because if the isotherm relation is linear, you have seen that delta q by delta c will be always m, it does not depend on the concentration at all. For non-linear absorption or for non-linear isotherm is for linear isotherm, absorption isotherm for non-linear adsorption isotherm solute velocity is depend on the solute concentration. So, concentration, but the low concentration, the linear absorption is valid. At lower concentration, that will lower solute concentration linear adsorption isotherm is valid.

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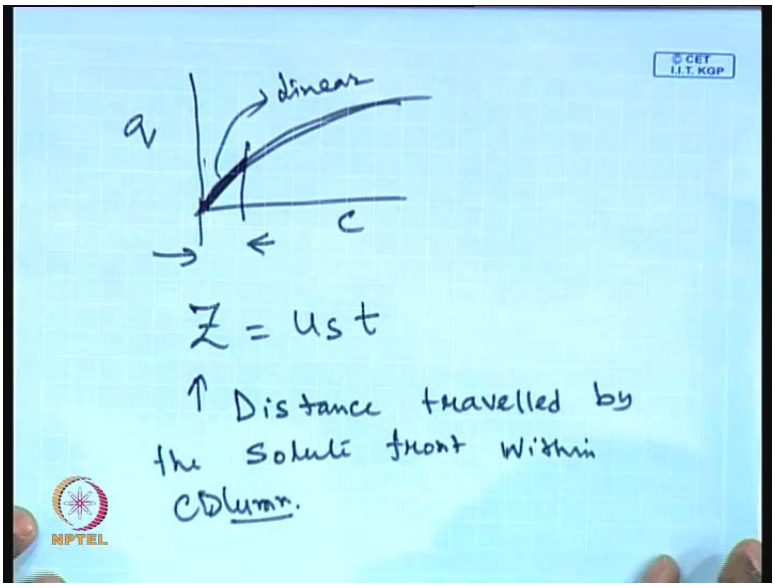

Also, if you look in to the adsorption non-linear adsorption isotherm so, this is the typically non-linear adsorption isotherm it will be something like this. It may be something like this. Now, if you talk about slower concentration again for example, in this range of concentration, the absorption can be considered to a linear part. So, the lower range of concentration the isotherm we can consider as a linear part of the non-linear overall it may be non-linear, but for a small region with in the very small concentration it will be linear. So, what is Z is the distance with travel along the column length so, Z is nothing but u s time t. If you put the value of Z of a total column length one term t will be nothing but the retention time.

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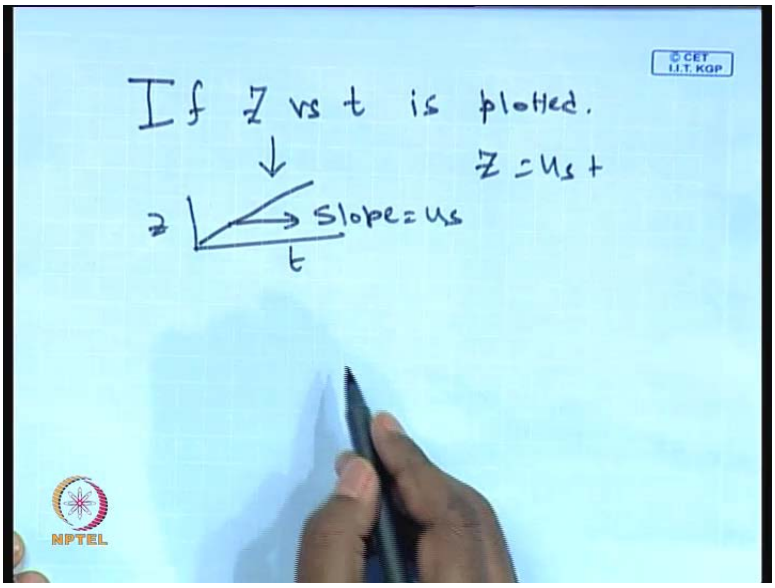

So, Z is that distance travelled by the solute for solute front you can say solute front with in chromatographic column. Now, if the Z is replaced by the l the t will be nothing but the retention time of the particular solute. Now, if you plot Z verses t. If Z verses t is plotted, you get a linear slow of u s. So, if it is plotted because u s Z is nothing but u s time t. Now, if you plot Z verses t, it becomes the linear and the slop is nothing but the u s the solute velocity, now, by looking into the Z verses t curve one can interpret the separation efficiency, how? That will be demonstrating in a next slide.

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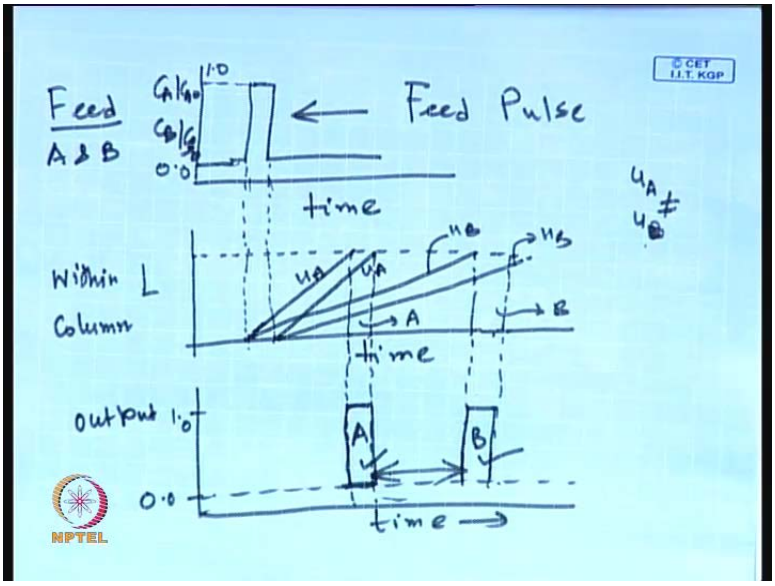

So, let us consider this curve this is the most vital curve and vital in a description of the chapter let say this is the feed and feed is composed of two materials let say A and B two solute are their A and B. Now, will plot here C A by C A naught or let say C B by C naught, what is C A naught and C B naught? C A naught and C B naught of the inlet concentration of species A and B in the column and C A and C B at the concentration of the exit of the column of both the species. So, this values is 1 this value is 0 will plot C A by C A naught and C B by C B naught verses time. In the feed phase, it give a at the at this particular instance of this particular time interval will give the pulse that contains C A naught c a and both the solute A and B; that means, you are injecting in to the feed in the feed sample will a injecting a pulse of the sample containing A and B.

So, therefore, it gives a region from 0 to 1. So, this is the feed pulse. Now, we plot L verses t, L is the length of the column. Now, these two species A and B will be having a velocity u A and u b respectively, depending on the nature of adsorption and so and so forth. So, therefore, the u A and u B will be different they will be not equal to they are not be equal. So, the slop of L verses time we already seen L verses time will be having the slop, slop of the individual solute velocity. So, the slope of the solute will be different because the two components are different. The expressions are defined will be getting this is this slope is u A and similarly, at the end of this injection time will be getting the same slop which of parallel to the other one and you will be getting u A.

So, at this particular time point will be getting only A component a out of the mix and A and B. Similarly, here the since the velocity of component B is different that of A so, this velocity slope will be different. So, that is in that case will be getting a slope will be here and at the end of the injection time will be getting another slope will be a exactly parallel to u B and u B getting a component B there. So, this component this period where will be getting A and this period will be getting B; that means, at this time t 1 will be getting only component A and at this time t 2 will be getting only component B and these two component will be separated out there be fractionated.

Now, if you so, this is with in the column, in the next I will just plot the below it this gives the output of column. So, again I will put it at one scale between 1 and 0. At this retention time reverses time in all the three v curves the x axis verses time. At this retention time you will having only component A. So, this will be a will be getting a pulse of component A here, this will contain only the component A. At this time t 2 will

be getting a pulse of component B. So, this is the pure component A, this is the pure component B, they will be separate out over a substantial amount of time and this separation will be depending on the nature of absorbent and nature of the mobile phase. That means, if you change the column from c 8 into c 8, then this difference may be shorten or may be avoidant. If it will be avoidant and then will be you can analyse them better. So, they will not overlap.

So, this is the principle of chromatographic separation. So, basically the solute movement will be defined for different solute in the chromatographic column because the adsorption intensity of the solute over the column at different and of course, the nature is also different. So, therefore, solute movement velocity will be different for the two solute and they will be appearing in the outlet stream which will be detected by the reflecting index. If the detected at different point of time which will be separated to a large extend. So that you can separate them out are you can them out quit easily.

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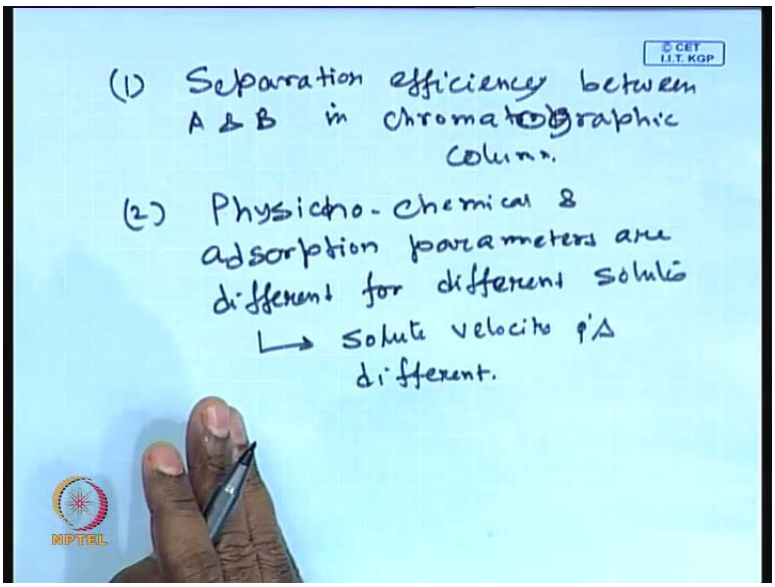

So, this chromatographic method is utilised for the separation number one, number two for the easy analysis. Now, let us look into the various salient features of this particular figure. This figure number 1 it demonstrates the separation efficiency between species A and B in chromatographic column. Number 2 is the physic chemical and adsorption parameter are different for different solutes Therefore, they are linear velocity will be different therefore, they are solute velocity is different so, because the differences solute

is different so, because of the differences solute velocity, you can have different concentration then the outlet at different point of time.

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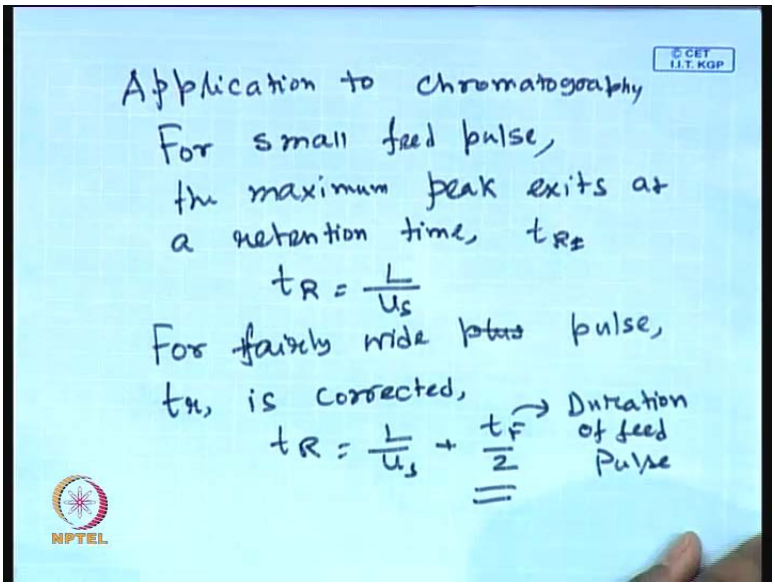

Now, let us look into the application on of solute movement theory to chromatography This is whole theory the up to that the figure you have discussed is known as the solute movement theory in the column. Now, let us try to apply at to chromatography. For small feed pulse, what you mean the small feed pulse? Because it means that I inject the feed over some microsecond let say thirty second let day five second. So, if the feed pulse duration is small it is called small feed pulse. The peak maximum exits, the maximum peak exits at a retention time t R 1 t R and this t R is nothing but L by u s. There will be retention time is length of the column divided by the solute velocity.

For fairly wide pulse the retention time is corrected. What is the corrected retention time? t r is corrected and corrected retention time is given as L by u s plus t F divided by 2, what is t F is the duration of feed pulse. If t F is very small for this case, this t F will be extremely small and t F it will be negligible. Otherwise, this correction has to will be added to the retention time. Suppose, you would like to inject the feed large period of time, then you have to take this correction t F by 2, t F by 2 should be added to the retention time.

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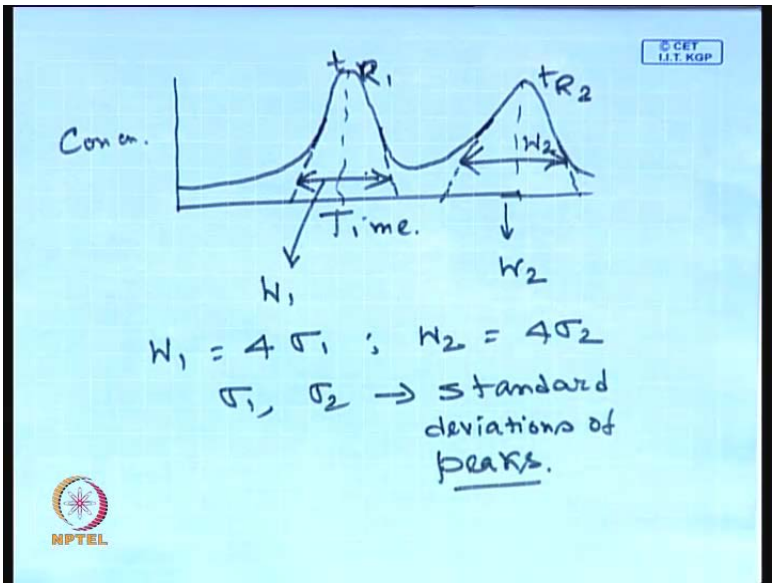

If you look in to the concentration verses time plot, then the look something like this. Suppose, there are two peaks you are going to get for two components A and B and this is t R 1 and this is t R 2 so, this is the retention time 1 and this is t R 2. Now, if you just plot if you just get to tangents here, this known as W 1 or the width. W 1 and if you just draw this tangents their let say the W 2, this W 1 is given as 4 times sigma 1 and W 2 is given as 4 times sigma 2; that means, width of the peak is connected to standard deviation of the peak so, sigma 1 and sigma 2 are the standard deviation of the peak of the peaks.

So, if this peak is very sharp, then you are going to get very good, the standard deviation is small the inaccuracy involved in your measurement will be extremely small. So, the interpretation is if W 1 W 2 are quit small, the inaccuracy involved in a interpret in your measurement will be small. If they are significant the larger; that means, the accuracy involved is a little bit more compare to the previous one. So, this is the generally of any chromatographic column of for then matter, how to get the separation and detect the concentration and the outlet of the chromatograph and analyse the thing.

Now, in the next class what I have do, I will just take up for a simple problem with various you know parameters for a examples it is isotherm characteristic and you know density of the solid materials, density the liquid material and the various properties will be giving. And I will just check for two solutes what will be the typical retention time it

comes out. And there are two things one is adsorption, another is desorption. Basically, suppose you are a having a column, which is not filled up with any liquid. And then you are passing a solute so, passing a solution containing the solute so, solute will be getting adsorb the earlier.

Then you will like to desorb the column, because you like to clean the column, so that it will be ready for the next experiment. So, then you have you sent the let say aqueous solution or the dissolute solution, and there will be desorption of the column. So, any way we will be look into a problem in more detail in the next class, and then we will move on to the next separation process, there is the ion exchange separation processes. Thank you.