Novel Separation Processes
Dr. Sirshendu De
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture No. # 36
Chromatographic Separation Processes

Good morning everyone. So, we have moving into the next separation process that is chromatographic separation process, but before that I would like to solve what have to discuss, in the last class. That I would like to solve one problem one centrifugal separation process it is a scaling up problem once we solve this problem will move on to the next topic of chromatographic separation process.

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So, let us first do a problem on scaling up of a centrifuge. Now in this problem it is will be again we are dealing with a slurry means again solid plus liquid and would like to separate the solid from the liquid stream using the centrifugal forces the it contains the solid particles of density 1200 kg per meter cube. It has to be clarified the centrifugation the solution density is given as 850 kg per meter cube the solution viscosity is given as 80 c p since the slurry contains huge amount of solid its viscosity will be more. And let us have a centrifuge let say centrifuge one, which are a bowl tubular bowl with r 2 this specification are given 0.02 meter and r 1 is 0 1 meter and height is given as 0.25 meter.

And we are going to use operating condition of r p m as 15000 revolution per minute and flow rate we are going to have 0.002 meter cube per hour. So, using this centrifuge now you would like to scale up this centrifuge.

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Looking for a centrifuge that can handle 1.5 times flow rate (q).
r_1, r_2 remain same.
b = Length of new centrifuge
Rotational speeds are same for both centrifuges.

Soln:

$$\frac{q_1}{\Sigma_1} = \frac{q_2}{\Sigma_2}$$

$$\frac{q_1}{q_2} = \frac{\Sigma_1}{\Sigma_2}$$

So, what we have to do now is that suppose we are looking for a centrifuge that can handle 1.5 times flow rate that is q the new centrifuge r 1 and r 2 remains same. And you have to find out the length of the centrifuge, length of new centrifuge assuming the revolution rotational speed is send the both the centrifugal, rotational speeds are same for both centrifuges. Now, let us look into the solution if you remember the you are going for you are looking for a particular parameter, which will be constant in both the cases what is the parameter? The parameter is terminal velocity due to gravity. So, if you equate that the then will be getting q 1 by epsilon 1 is equal to q 2 by epsilon two this is the scaling up equation that we have already talked about.

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So, q 1 divided by q 2 is nothing, but epsilon 1 divided by epsilon 2. Now, if you remember the expression about the epsilon the sigma value the sig the sigma is basically, it talks about the geometric. And characteristic of centrifugal only it does not talk about the characteristic of the fluid and the solid system, so therefore, if you look into the expression of sigma it becomes omega square pie b r 2 square minus r 1 square divided by 2 g l n 2 r 2 divided by r 1 plus r 2. So, if you remember problem statement r 1 and r 2 and omega are same for the two centrifuge is that talking about. And discussing and only the parameter that will be varying is the length of the centrifuge therefore, q 1 divided by q 2 will be nothing, but b 1 divided by b 2 all the other things being other value terms remaining constant assuming equal they will cancel each other.

So, therefore, q 1 by q 2 is equal to b 1 by b 2 and if you put the values of q 1 by q 2 is what is q 2? q 2 is nothing, but 1 point times q 1 so, this becomes 1 by 1.5 is equal to b 1 b 2 so, therefore, b 2 will be 1.5 times b 1. So, within the value of b 1 is .25 meter so, it becomes 0 .37 meter b 2 so, the length of the mu centrifuge becomes 0.375 meter and via is the whole centrifuges .25 meter. So, if you select the centrifugal same dimensions of r 1 and r 2, but if you select a length of .375 they need can hundred flow rate, which is one point five times more than the flow rate then we are talking about the flow rate of the earlier centrifuge.

Now, this example gives an idea how to scale up the various geometrical parameters of the centrifuge for example, if you like to tube the value of the constant, if you like to varying r 1 and r 2 that gives an idea, how to defined parameters will be the geometrical variables will be this determined when you are going for a scaling up operation.

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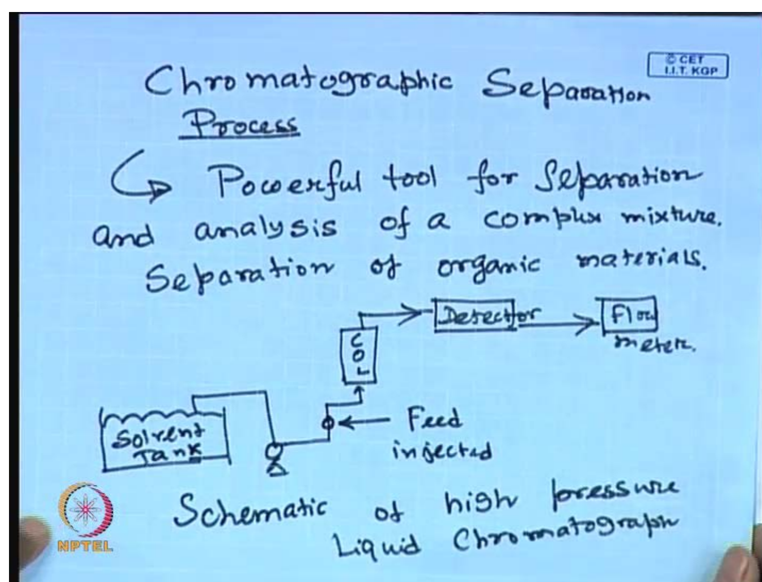

So, this gives the complete idea of scaling up of centrifuge. Next will move on to the next separation process that is chromatographic separation process. Now, it is a extremely powerful to for separation. And analysis of complex mixture this is the powerful tool for separation and analysis, of a complex mixture typically talking about the separation of organic materials. And yes an analytical high pressure liquid chromatographic I will just drive semantic of a first will be having a solvent tank, this is a solvent tank from the tank there is the pump, which pumps the liquid in to the column.

So, you will have a column and their you pump the solvent into the column and some here in between before entering in to the column you inject the feed. So, feed is injected the effluent the feed mixed of with a solvent it goes through the column. And the effluent will be coming out through a detector. And this detector is some logic reflecting in the detector or some time it is a will be visible spectrometer. And then it goes to there is a flow meter out there to detail the flow rate of the solvent. So, this is a typical that schematic of a high pressure liquid chromatograph. Now, a typical chromatograph will contain certain features.

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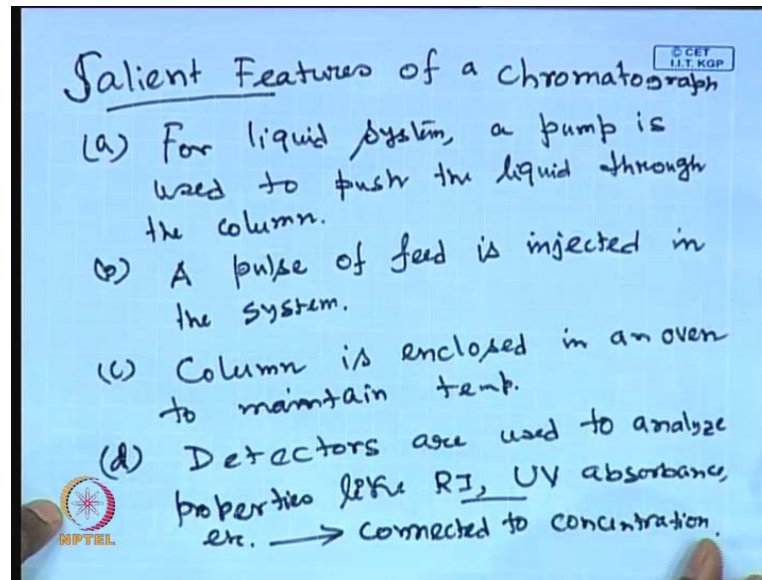

So, let us note down the salient features of a chromatograph. So, first which is liquid system, we must be having a pump to push the liquid through the column, for liquid system, a pump is used to push the liquid through the column. Secondly, a pulse of feed will be injected in to the system. So, we are not injecting in the feed continuously we just injecting a pulse of feed is injected in the system. Thirdly the column is offered enclose in an over and will maintain the temperature column is enclosed in an oven to control or maintain temperature. Lastly you must be having a detected that analysis some properties like a optical index you will observance etcetera.

So, detectors are used to analyse properties like refractive index U V observant etcetera. And this property is this value of the reflective induction gives you observance value exedra, are connected to concentration. So, one can have the value of reflective in one can have a pure solution and get a calibration call and that those can be utilise in order to find out the concentration of the actual sample.

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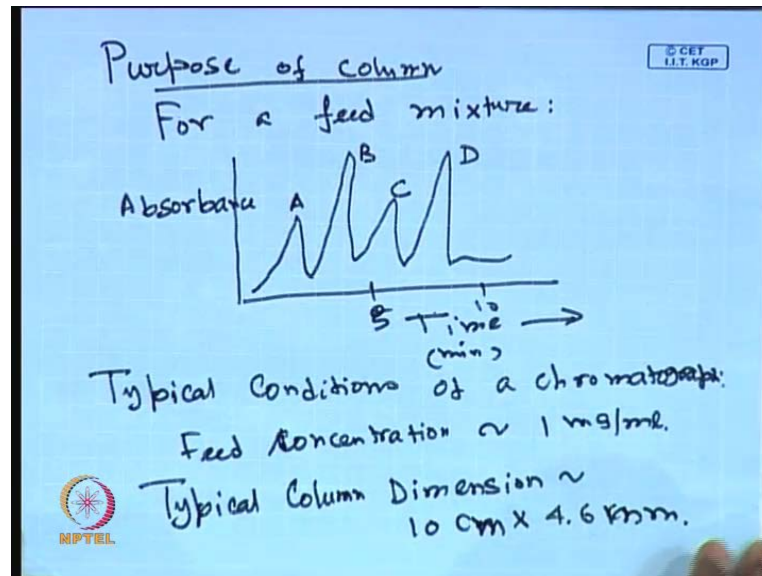

Now, let us look in to the purpose of the column suppose you will be having a feed mixture that means mixture contains difference kinds of components so for a feed mixture. Now, it will be showing suppose, a mixture contains there are 4 5 components then it will be getting 4 5, it is column correspondent to which component. So, the resolution will be depending upon how go to your column it is. If you look into the observance value and time of that will the residence time of which of the material is going to the column will be getting various species. And the area in the each peak will correspond to know let say this is 5 minute and it let say minute 10 minute.

So, this peak was corresponded to component A this peak correspond to component B C D. So, various components will be having various properties and will be look in to why this property will be the will basically, the cause to have difference residence. So, at different residence time you will be getting peaks of column corresponding component. Now, the area under this curve will diffuse the value of the concentration now typical concentration of a feed otherwise look into the typical conditions of a chromatograph. The feed concentration will be estimate daily feed concentration will be in the order of one p m that means, now it is less than that 1 milligram per m l right to be extremely, small and typical column dimension that we have the talking about that will be in the order of 10 centimetre mull in to 4.6 millimetre.

That means, diameter 4.6 millimetre and length is around 10 centimetre that is typically a column dimension it contains it a paid of materials.

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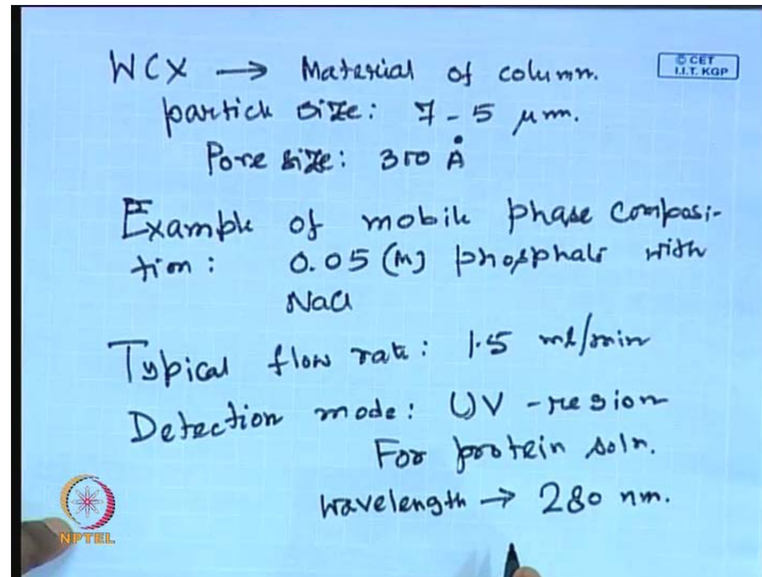

Which is nothing but the material of column W C X is a typical material of column and the particle size will be in the order of 7 to 5, 5 to 7 micron basically. And the pore size inside the materials will be 300 Armstrong it will be in that order of magnitude the possible mobile phase composition can be any field that means, about the solvent composition. And just give an example of mobile phase composition the typical example of mobile phase composition is 0.05 molar phosphate width sodium chloride, we can have various other mover is composition as well for a typical for different you know uses. Typical flow rate that you are talking about will be in the order of 1.5 m l per minute from given this figure, to identify the what do the typical value is of various separating condition chromatograph? The detection mode is U V region ultra violet region and for protein you have detect.

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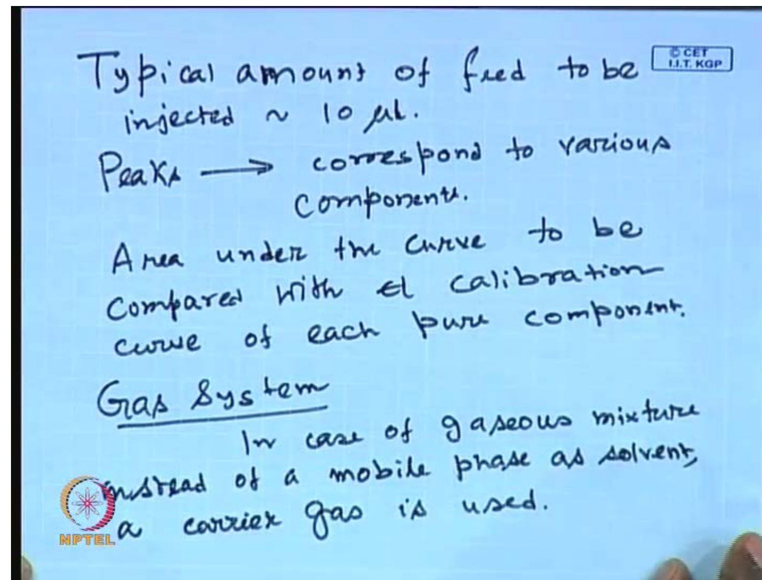

So, depending on the solute we have going to analyse the wave length of will be detection will be used, for protein absorption of protein solution. The wave length of U V are ultra of violet is set at 280 nanometre that is a typical value. And the how much the amount of feed that we are going to inject the typical amount of feed that, we are going to inject will be extremely small give in the order of micro litre will be around 8 micro meter, 10 micro litre amount of feed to be inject will be 10 micro litre peaks in the response the correspond to various component.

And area under the curve to be compared with calibration curve of each pure component that means, if you are having a mixture of 4 or 5 components then you have to take the pure component of each species. Then inject 10 micro litre of each pure species in to the h p r c column in that for the whomever running pure component you are suppose, to get a one peak. That peak cause to a pure component is and use the, and you have to use the same mobile phase composition of the mixture. That means, you are using same mobile phase know composition for each and every pure component and area under the curve.

So, after getting each and every injecting can every pure component you are going to get up peak single peak for each of them. If it is let say 99 percent pure or 98 percent pure. Now, the area under so for the now what we can do? We can inject you can take various concentration of the pure component. And injected that means, the area under the curve at a particular attention time where the you know the peak will be appearing that will be

graving in area. So, therefore, is area under the curve will be basically function of concentration of the component that we are talking about.

So, now, you take the concentration you know the concentration and you know the area and a plot area verses concentration that gives the calibration curve of p m component similarly. Suppose, you are talking about five components in a mixture you inject different concentration of this five materials into the column. And get the calibration curve of every five complete five components now, when you put the mixture in the in the same mobile phase composition you put the mixture you inject the mixture in to the column. And will be getting let say five peaks one after another and the area under the curve will be you can the software itself, will give the area under the curve value you can go to each and every calibration curve corresponding to a every component.

And can get the concentration values that how it will be the working? Now, let us look into the working principles of so, that how one will calibrate and get the values of mixture the concentration in a typical chromatographic column. Now, let us look in to the underline principle of chromatographic operation or chromatographic separation process. Now, let us there are various system, so one can have gas gaseous system one can have liquid system, one can have a the various types of system, it is will talk about the gaseous system in case of gaseous system, instead of a solvent or instead of a solvent mixture. You will having a carrier gas in case of gaseous mixture instead of a mobile phase is as a solvent the mobile phase or solvent in case of liquid right in this case the mobile phase will be gaseous a carrier gas is used.

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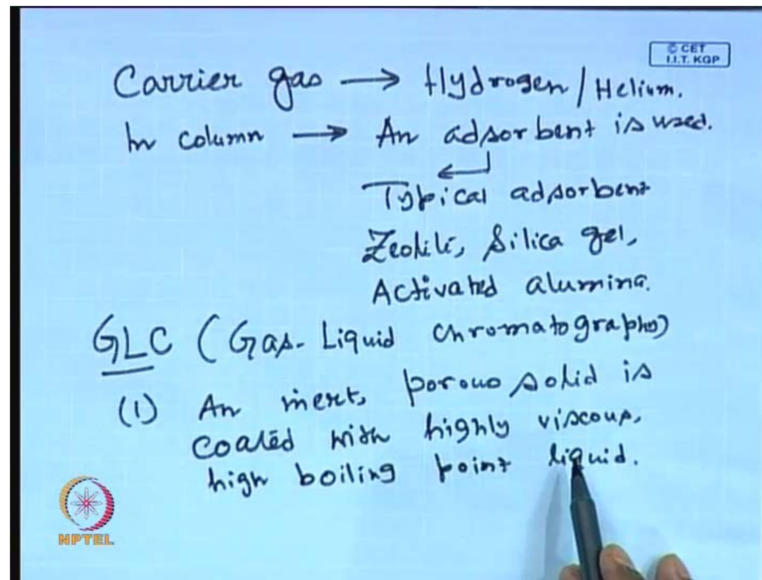

Now this carrier gas can be hydrogen or helium an in column, an a absorbent is used. An a typical absorbent that we are talking about and Zeolite, Silica gel, activated alumina etcetera. Let us you look in to the gas liquid chromatographic GLC. GLC is nothing but the gas liquid chromatographic in gas liquid chromatographic, and inert porous solid is coated with the discuss high volume liquid. The first feature is that an inert porous solid is coated with highly viscous high volume point liquid.

So, what is the purpose? The purpose is basically this phase, this liquid phase that is highly viscous it is almost a stationary phase that means, it does not move on the open of the solid sulphured tick to the solid surface number one. Number two is since it is having, may it is volume point is quit high then you can go for a higher temperature operation as well. So, it will not corporate.

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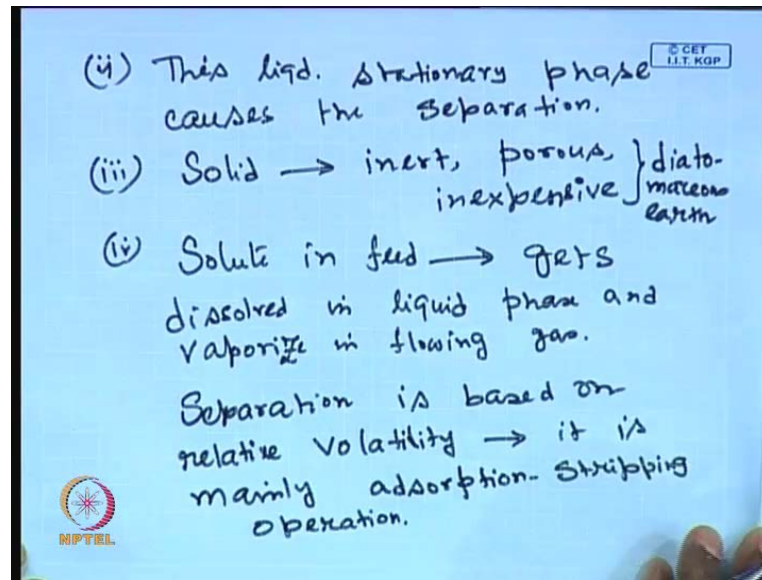

So, therefore, this stationary phase will cause the separation, in a gas liquid chromatographic the sepal. This stationary phase, this liquid stationary phase that will be encompassing in the solid particle causes separation, stationary phase causes the separation. Thirdly the characteristic of the solid should be inert. Because the liquid the stationary phase is basically, the separation cause in phase the solid has to be inert, otherwise it will be interfering inert to the mass transfer should be porous. It should be inexpensive it is a typical characteristic of the solid, example of a solid is diatomaceous earth, it is basically a material.

So, that is highly porous and it is easily available and solid in fluid can dissolved in stationary phase. So, solute in feed, but it does it get dissolve in liquid phase, and then vaporize in flowing gas. So, what is the separation is therefore, is based on relative volatility and it usually, and observe from stroking operation separation is based on relative volatility and it is essentially it is mainly absorption and stripping operation. Therefore, you are absorbing the solute is absorb in the stationary phase, on the solid and whenever passing the gas the solid is desorbs are, it is getting strip of from the base station then coming in to the gaseous phase.

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Disadvantages of GLC

(1) Slow evaporation of stationary phase occurs.

→ (1) Column criteria is changed

(2) Contaminates the product.

Capillary Gas Chromatography

A glass/fused silica capillary is used with a coating of adsorbent or high boiling solvent on the wall is used.

Now, let us look into the disadvantages of G L C, of gas liquid chromatographic number one is. The stationary although it has a high volume point it is really, evaluated porous slow evaporation of stationary phase occurs. So, what it does it affect? It leads to harmful affect one is the column criteria is changed. Because it is the capability initially it was a capable it was having a capability, but if we vaporise to some exchange it capably decreases. So, column criteria is changed and it contaminates the product, if the stationary phase is the liquid phase that is producing a film over the solid. If it evaporates it act as a contaminant to the gaseous stream right in the product stream.

So, goes in to the production stream, so it act as a contaminant. Now, let us look into the capillary gas chromatographic this a it is say a glass or fused silica capillary, is used in this case a glass are fused silica capillary is used with a coating of absorbent or high boiling solvent on the wall is used. But since the stationary phase quantity amount is less it has a it is a capacity is limited.

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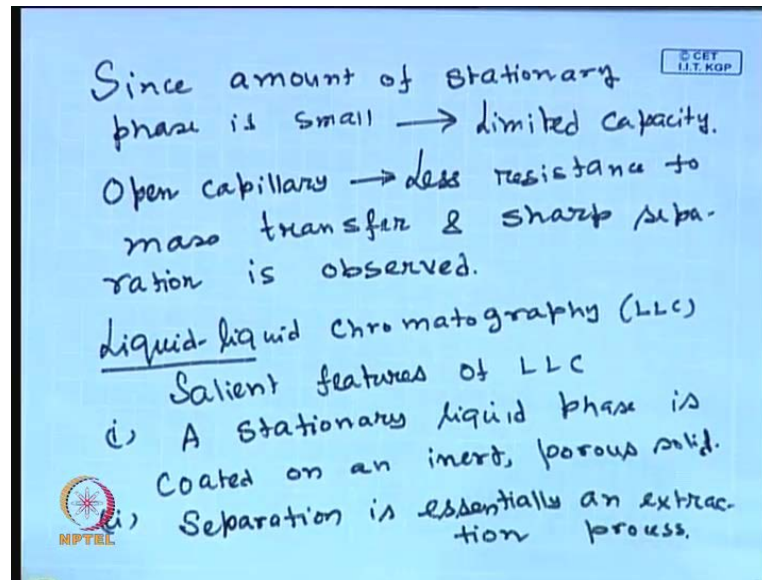

So, the disadvantages since amount of stationary phase is small is capacity is limited. So, it has a limited capacity on the other hand open capillary it has a little resistance to mass transfer, less resistance to mass transfer and sharp separation is observed. So, there is capillary gas chromatographic. Let us look in to another chromatographic that is called liquid, liquid chromatographic of L L C. Now, the salient features of liquid, liquid chromatographic or number one a stationary liquid phase is rotate overall inert, porous surface. A stationary is just earlier liquid phase is coated on an inert, porous solid number one separation is essentially an extraction process.

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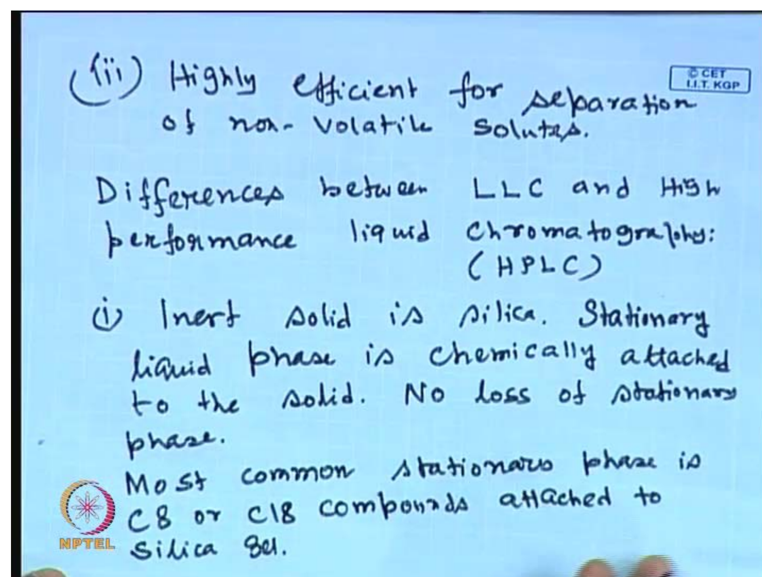

And it is useful for separating non volatile solution, highly efficient for separation of non volatile solutes. Now, let us look in to the effluence between L L C and modern high pressure high performance liquid chromatographic of H P L C. Differences between liquid, liquid chromatograph and high performance liquid chromatographic this high performance liquid chromatographic the other name the in short is known as H P L C. The first defined is the inert solid is silicon both the phases, inert solid is silica stationary liquid phase is chemically attached to the solid. So, it is basically column characteristic, so these materials are in build within the column one here purchasing the column.

The whole column contain is solid as well as the embedded liquid along with it. So, we are not do anything basically, so your basically passing the solute along with the solvent within the column. So, stationary liquid phase is chemically attached to the solid. So, therefore, it is there is no loss of stationary phase. Since it is chemically attached the attachment is stronger than in physical attachment young option. So, there is less probability of using this stationary phase when the solvent will be going through it. So, most common stationary phase is C 8 or C 18 components attached to silica gel.

That means, you having carbon component of having 8 carbon account or 18 carbon accounts that, why those are attached to the silica gel, that is a inert porous solid that is why this columns are termed as 18 column the tumbles C 8 column. So, you must ordering for the C 8 column or my ordering a C 18 column that means, the C 18 components will be in the liquid phase. And they will be attached the chemically they will bond a chemically over the silica gel particle and typically the solvent this water.

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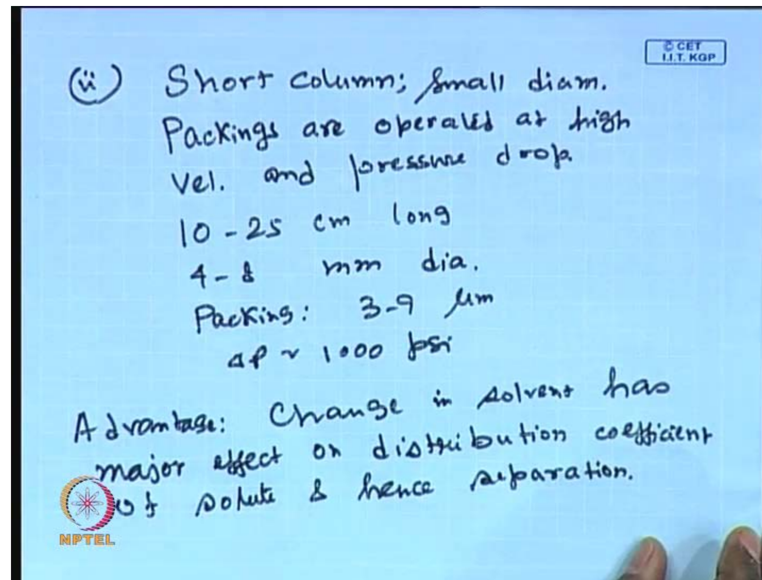

The second criteria second feature is that the short column have very small diameter short column. And they have small diameter packing or operated at high velocity and pressure drop. So, since the column itself is very short and the packing of the very closed. So, the operating pressure drop called high, in the high performance liquid chromatographic. The typical conditions are the column is 10 to 25 centimetre long 4-8 millimetre in diameter, internal diameter typical packing dimensions are 3-9 micron and delta p will be around thousand p s i. Since the packing materials are so small in diameter the form a closed pack material within the column.

So, therefore, in order to affect a flow you must be having a very high pressure drop, and the high pressure drop will be in the order of 1000 p s i. But the what is the advantages changing solvent has a major affect on distribution coefficient hence on separation that means, if you change the solvent instead of what the it will use some other mobile phase for example, oxygen nitrate. So, change in solvent has major affect on distribution coefficient of solute and hence separation. So, if you can suppose, you are not get with a particular solvent you are not getting in the required separation or. So, that the things so, this are getting the around almost super on position.

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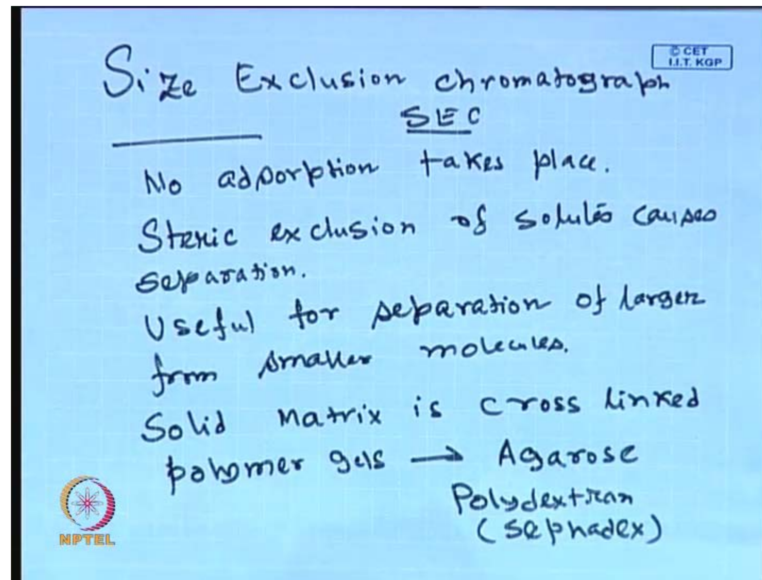

So, you can change the solvent, you can change the flow rate as well as slightly and then, we can when the column. And see we that this two peaks are different are coming one have to another. Now, is the sufficient cap you have to overlapping next we just look into the g p c or solid exclusion chromatographic they offend known as S E C. Now, in this case no adsorption, take place satiric exclusion of the solute place the most important role, what is the satiric exclusion is nothing but the size exclusion. That means, if the particle is has largest compare to the agars it will excluded, it will not going to the force streak exclusion of solutes causes separation.

So, this is useful so therefore, this method is extremely useful for separation of larger molecules from smaller molecules. The solid matrix is cross linked polymer gels for example, agarose sephadex polydextran this is often known as the sephadex. So, this materials they are used for preparation of the solid metrics are the at this solid metrics, are kept in the column and the solid and the exclusion of the depending on the size the lager particles will be separated from the smaller particles. The smaller particles are allowed to flow along the solvent through the column the larger particle will be excluded.

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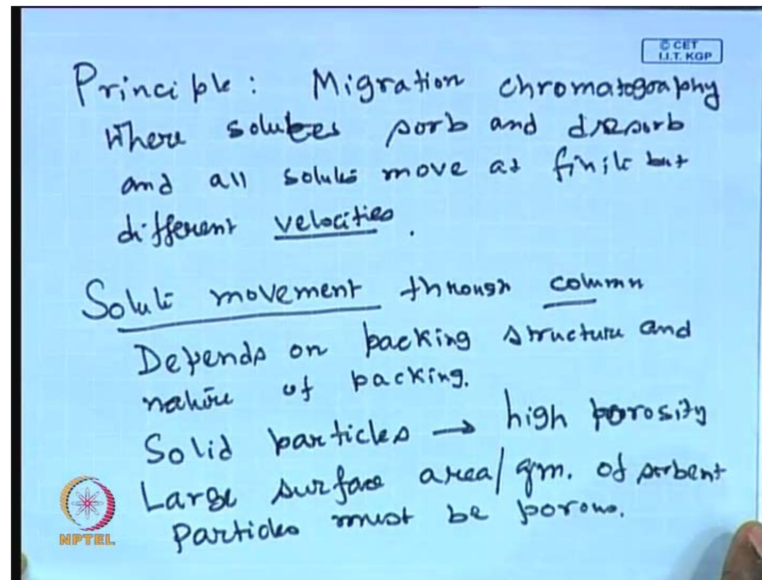

So, the principle of working, principle it is a also known as the migration chromatography, where solutes sorbs and desorbs and all solute move at finite, but different velocities. So, this is a general principle of any a chromatographic column. Now, let us look into the solute movement system, solute movement through the column this entirely depends on the packing structure on the nature of the packing. So, the solute movement the first factor is depends on packing structure and nature of packing. Solid particles should be solvents have been high porous, that mean solute particle that is those are present into the column. The must be having high porosity their they should have large surface area per gram of the solvent, this is the typical characteristic large surface area per gram of solvent.

So, that the absorption capable capacity will be more now particles must be porous where the particle must be porous, because it will if the particles the porous it will affect more separation. Because some particle will be absorb on the outer force, as well as inner force there are loss of force. The going in to the structures, are solute will be not only absorb on the surface, they will be going in to the force. And they will be getting absorb their so separation will be more or it will be more efficient.

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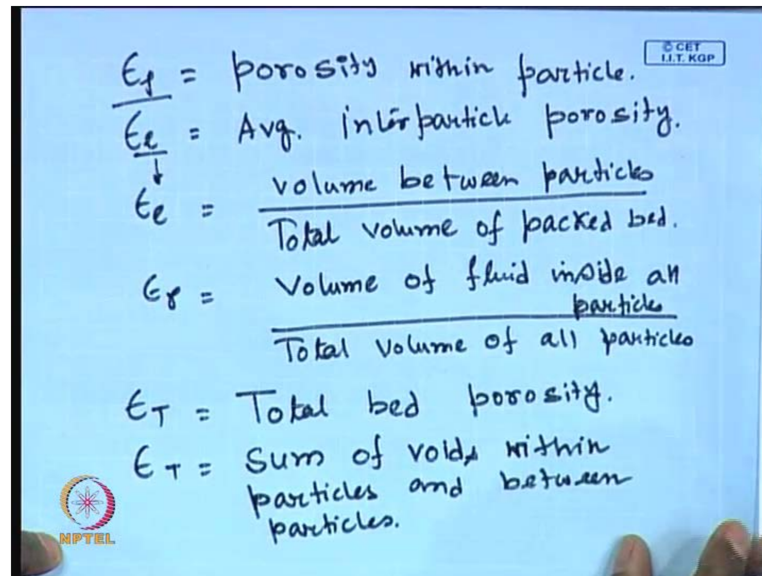

So, let us had some definition of porosity of the particle epsilon p is the porosity within particle, epsilon e is the average inter particle porosity. So, epsilon that means, this is a epsilon p is inter particle porosity that means, this porosity correspond to the porosity of the particle and epsilon is average inter particle porous that means, this porosity between the adjacent particles. So, this inter particle porosity, and this is epsilon p nothing but inter particle porosity that means, epsilon p correspond to particle porosity and epsilon e correspond to inter particle porosity. So, that is the porosity that exist between the adjacent particles. So, you can have the definition.

Now, easel epsilon e is basically, volume between particles this is epsilon e divided by total volume of the packed bed epsilon p is volume of fluid inside small particles is the particle porosity volume of fluid inside all particles divided by total volume of all particles. So, therefore, once you defined this to quantities you will be in a projection to defined. The total bed porosity epsilon T is total bed porosity and total bed porosity is defined as some of voids with in particles and between the particles. So, there is the total porosity.

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So, this is defined as epsilon e There is the inter particle porosity plus 1minus epsilon e. So, there is the solute fraction epsilon e is the inter particle porosity 1minus epsilon is the void fraction of the solid right, and they should be multiplied by the epsilon p right. So, this is the void in of the particle use an each particle will be having a porosity epsilon p. So, it will be multiplied by 1 minus epsilon in to epsilon p. So, once you defined the this bulk density can be defined, the bulk density is defined as rho bulk is equal to 1 minus epsilon e Times rho p plus epsilon e Times rho f.

So, epsilon e is basically the inter particle porosity where it will be occupied by the rho f the fluid rho it is the density of the fluid. And rho p is density of the particle, so epsilon is the void volume of the space inter particle phase. So, should be occupied by the feed it will be multiplied by the density of the fluid 1 minus epsilon e is basically, the particle of the occupied the void fraction occupied by the particle it should be multiplied by the particle density. So, total bulk density is defined this way it is basically, a and whiter average of the particle density at the fluid density, and the white fraction proportional to the void fraction. And rho p the particle density is defined as 1 minus epsilon p rho s plus epsilon p rho f what is this? rho s is the crystalline density after crushing, and compressing the solutes without any pore, so in the particle porous.

So, let us two parts one is the entirely solid part what is there is know that is the crystalline density, what is the crystalline density you cross the particle compress it. So,

the there is no pore, there exist no pore. And find out the density there is the density of the absolutely solute particle, and some part of since it is porous in structure the porous what fraction will be again occupied by the fluid, that mean multiplied by the rho. So, again particle density will be an waited average of the density of the fluid and density of the actual density of the solid. And the what are the void? The voids will be proportional to the void fraction of which per, which you know system that means, the porous part and non porous part.

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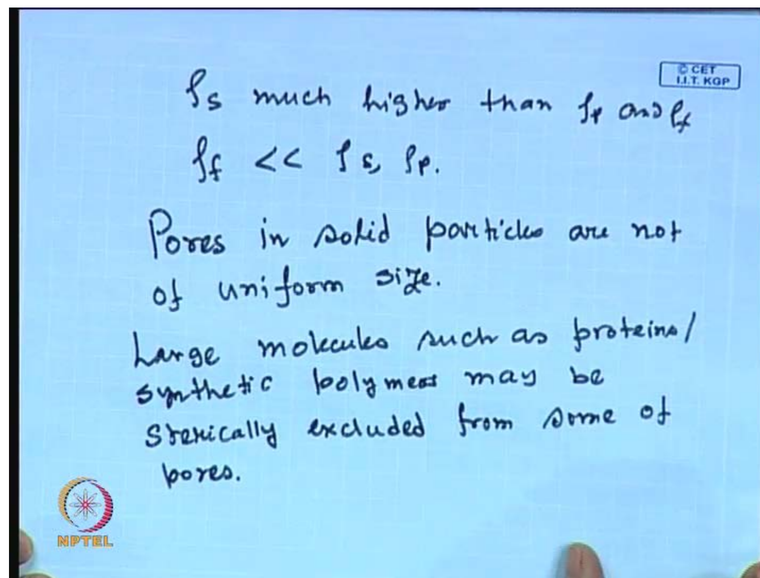

Now, obviously, the crystalline density rho is much higher than rho p and rho f and rho f rho flute is much less than rho s and rho p. And also the pores of are not uniform size the we are talking about the pores with in the solid particles. Pores in solid particles are not of uniform size that means, they are not straights cylindrical pores even not cylindrical they are not of they may be tracheal, they may be of different dimensions.

So, large molecules may be statically excluded from the pores therefore, it is also possible, always possible that large molecules cannot going side the pores, because the size is more. So, by so this is called strerically excluded, so size exclusion large molecules such as proteins synthetic polymers, may be strerically excluded. Some of the pores they may not be strerically estimation all pores, because the pores not of uniform size then we be a flow rate some of the pores, which will be having it is the die the typical diameter, which will be less than the diameter of the materials.

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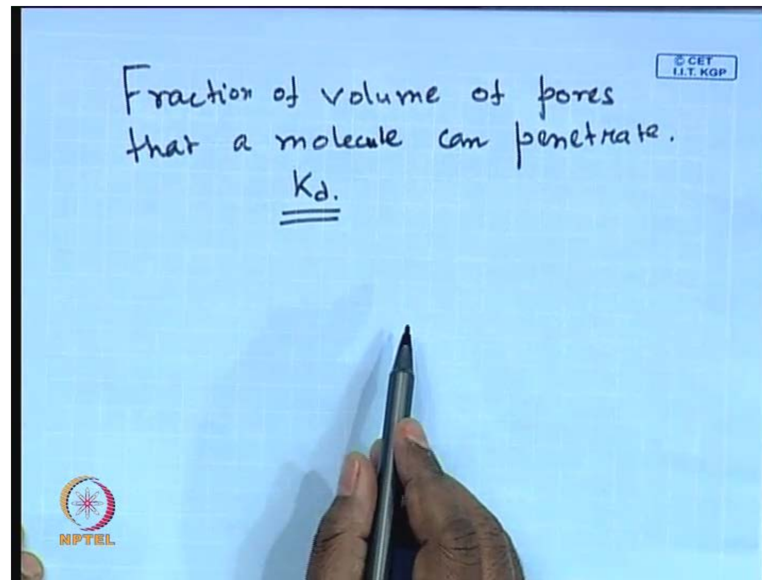

So, let us defined this fraction is basically nothing but by the fraction of volume of pores that a molecule can penetrate, this fraction let us called it is K d. So, K d is the fraction of the volume fraction of the pores where a molecule can penetrate. So, the other pores cannot penetrate, so anyway so they you basically, defined some of the will be useful to look into the solute movement it to the column of the chromatographic. So, by looking in to the solute movement and by looking in to the time required to cross the particular column length you will be finding out that, because of the difference velocity of void the velocity difference will occur, because various solute will be absorb various in different wise on the absolvent.

So, they are velocity will be obviously, different, because of this velocity will be different the residence time of the particular components through the column will be different, what are the mean? That means, the stream that is going out of the column will be having a particular component reach, for the at the particular time. After that it becomes dilute and then after some time it, becomes reach the another component that means, you are going to get peak at different residence times that means, you are going to separate this solute the differently. And you can identify them easily or analyse them quit accurately. So, will be looking into the theory of the solute movement theory in more detail and of course, will be taking of the example to compute this residence of various solute in a chromatographic column in a coming class. Thank you.