**Novel Separation Processes**
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**Lecture No. # 38**
**Ion Exchange Processes**

Good morning, everyone. In the last class what we have seen is we have looked into the basic principles of chromatographic separation processes, and what are the various chromatographic processes, for example, gas-liquid chromatography, high-performance liquid chromatography, liquid-liquid chromatography, L-L C, the advantages and disadvantages of various chromatography processes, the basic principles of operations of chromatographic and how the chromatographic separation will occur. For example, it basically depends on how the solute in the liquid phase will be transferred into the solid phase that is an adsorbent phase in various manners.

Therefore, the concentration of the solute, two different solutes that will be coming in the output stream, will be occurring at different points of time, because the velocity of the liquid front will be moving in the different velocities, depending on the nature of adsorbtional particular solute towards the solid-solid phase that is the adsorbent phase.

So, therefore, the retention time will be different for two different solids, solutes and one can have an estimation, a quantitative estimation that will be detected by a detector like either it will be a refractometer, or it will be observance in U V range, ultraviolet range, and that will be giving you the quantitative analysis of various solutes present in a liquid solution, which will be a extremely dilute condition. If you want to analyze a concentrated solution, you have to dilute it to an appropriate proportion and then you have to inject into the chromatographic column.

Now, in today's class, we will be looking into another separation process that is Ion-Exchange separation process. But, before that, I would like to solve the problem on chromatography principles, so that things become clearer to you in order to know how these operations will occur in principle.

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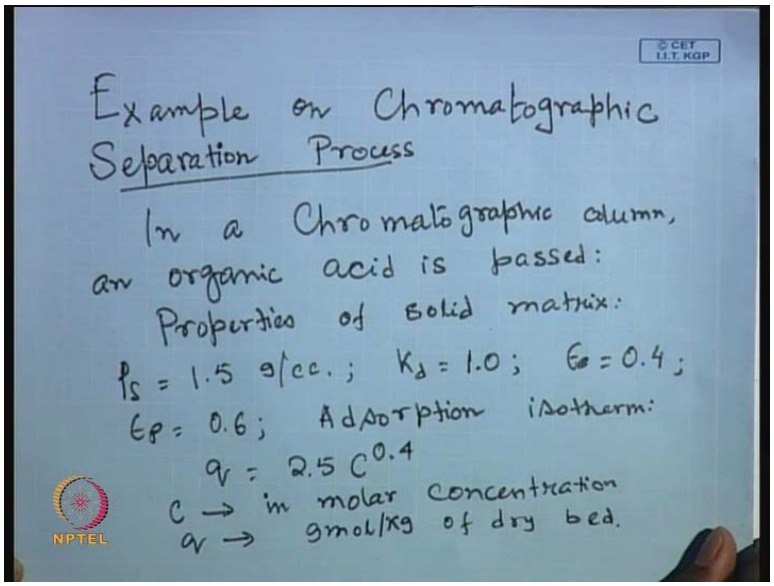


Let us solve a first example on chromatographic separation and then we move onto ion exchange process.

We have a chromatographic column and in a chromatographic column, an organic acid is passed. The properties of various parameters of the solid matrix are given. The rho is the density of the solid is 1.5 gram per c c, per centimeter cube.

The parameter value of K d is 1.0, in this particular case. Epsilon E, the bed porosity is 0.4, it is given, and epsilon p that is intra particle porosity that we have defined in the last class that is 0.6 and epsilon e is basically inter particle porosity that is basically bed porosity. The adsorption isotherm of the solute is given. It is given as q and equal to 2.5 C to be power 0.4 that is the adsorption isotherm of the solute, and C is in molar concentration and q is having a unit in gram mole per kg of dry bed. Now, we have to do several calculations, these calculations will be...

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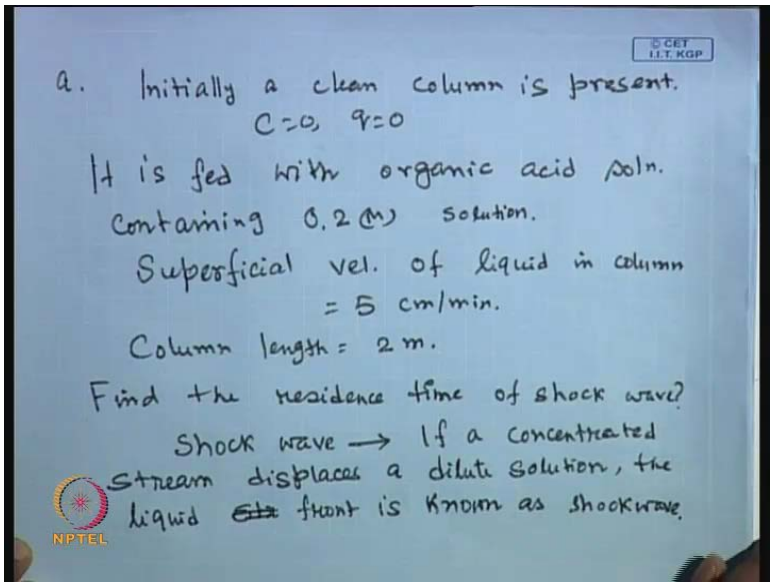


First calculation is initially, we have a clean column. Initially, a clean column is present; that means, in that clean column C is equal to 0 and q is equal to 0. We are not putting any solute containing liquid and there is no solute that will be adsorbed in the solute phase. The clean column is fed with organic acid solution containing 0.2 molar solution. You have a pump to pump the liquid through the column, by setting the pump you can have the velocity of the superficial velocity of the liquid front that is moving into the column. You can set it basically; superficial velocity is in operating condition.

So, you can set your field velocity in the column. The velocity is given as 5 centimeter per minute, velocity of liquid front of liquid in column, it is given, and this is 5 centimeter per minute. Column length is given; it is a big column, the column length is two meter. So, it is around 6 feet. Find the residence time of the shock wave.

What is the shock wave? Shock wave is, basically, if we inject a concentrate stream to displace a dilute stream then a shock wave will result. So, it is like a shock wave. You do not have anything. Suddenly, you push 0.2 molar solution. So, there is nothing initially, zero concentration was there. Now, you have a 0.2 molar solution. So, the effluent that is the elutant that is coming out of the column, it will be having the concentration very high. So, it is like a shock wave and we call that wave as a shock wave. The moment of this concentrated liquid front is known as a shock wave. If a concentrated liquid displaces a dilute liquid in the column, then the liquid font is known as the shock wave.

If a concentrated stream displaces a dilute solution, the liquid front is known as shock wave.

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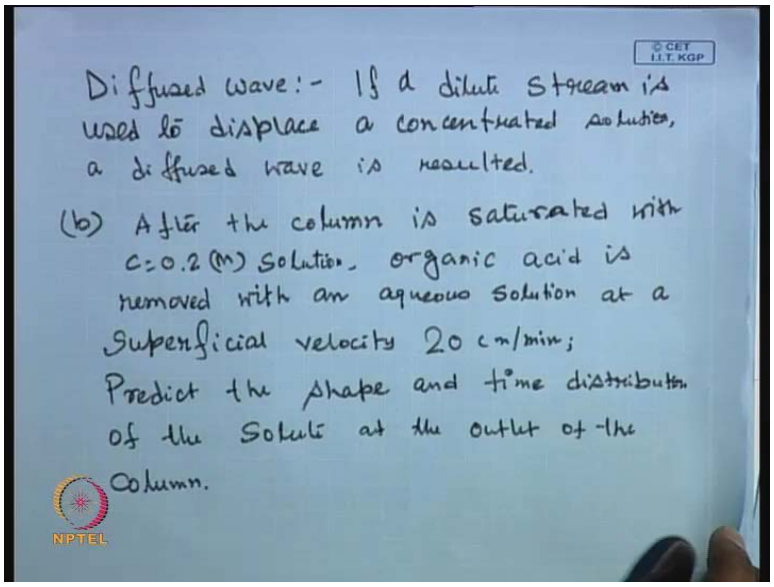


On the other hand, what is the diffused wave? There is a shock wave and diffused wave. The diffused wave is the other thing, the reverse one. If a dilute stream displaces a concentrated stream, then what will happen at the exit is you will be getting the concentration of the particular solute, which is decreasing slowly. If you do not have anything there, suppose you have a dilute stream, now you displace the particular liquid in the column by a concentrate stream. So, initially you will be getting a huge concentration at the outlet. So, that is called a shock wave.

On the other hand, if you have a concentration interrupting in the column, and you are feeding a dilute stream, from the bottom, using the pump and displacing the liquids, the liquid that is in and that was interrupting the column. Slowly, its concentration will go down at the outlet. So, that is called a diffused wave.

If a dilute stream is used to displace a concentrated solution, a diffused wave result is resulted. So, the first problem we had that first part is you have to find out the residence time of the shock wave. The second part (Refer Slide Time: 09:44) is after the column is…. So, after some time the column will adsorb all the solutes that are present in the stream and after some time the column will be totally saturated. Then you have to regenerate the column. So, you have to send another dilute stream to regenerate the

column; that means, whatever is being absorbed, so that the things will be desorbed and you will be getting almost the previous earlier performance.

After the column (Refer Slide Time: 10:17) is saturated with C is equal to 0.2 molar solution, organic acid is removed with an aqua solution. Here, the dilute stream is nothing, but, the aqua solution at a superficial velocity 20 centimeter per minute. Just check that in part a, we are injecting the column with a lower velocity of 5 centimeter per second during the absorption cycle, on the desorption cycle we are sending the aqua solution at a velocity is 4 times the earlier one, that is 20 centimeter per minute. Then predict the shape and time distribution of the solute at the outlet of the column.

So, first part concerns with the shock wave the second part concern with the diffused wave.

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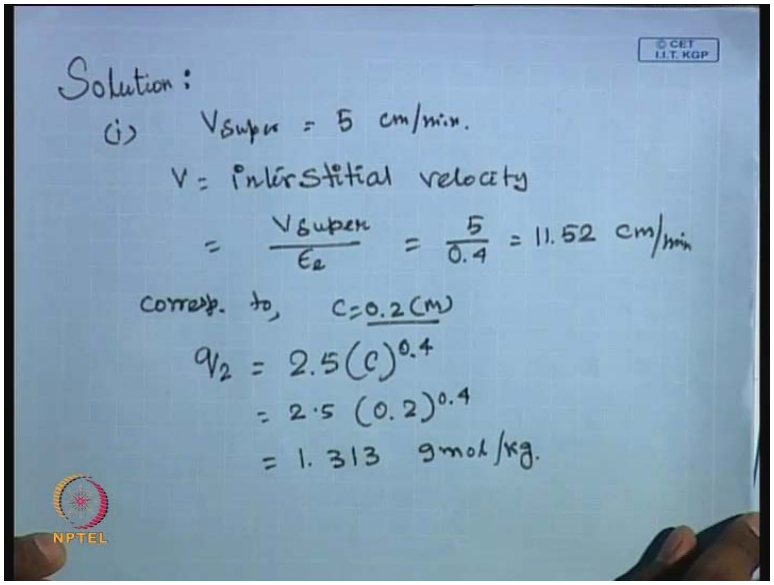


We will look into the solution. We have the superficial velocity for the shock wave shock wave is 5 centimeter per minute, and let us have the velocity and interstitial velocity that is the velocity of the liquid moving to the inter particle pores, will be different. So, these velocities have to be different. Will it be more or less? It will be more, simply because the area of cross section. The superficial velocity is defined on the area of cross section of the column.

On the other hand, the interstitial velocity will be defined by the area of cross section of the, let us say internal pore, inter-particle pore. Since, the cross section will be less; its velocity will be high. So, therefore, it has to be divided by the inter particle porosity. So, interstitial velocity v is given by v superficial divided by epsilon e that is the inter particle porosity that is given as 0.4 (Refer Slide Time: 13:10).

So, 5 divided by 0.4 and these turns out to be 11.52 centimeter per minute. Now, corresponding to C is equal to 0.2 molar. If you would like to find out what is the amount of solute that will be observed within the solute phase is given as q 2 is 2.5 C raise to the power 0.4. So, you would like to find out what is the value of q corresponding to this concentration of the solute in the liquid phase. So, these turns out to be 2.5 into 0.2 raise to the power 0.4 and these turns out to be 1.313 gram mol per kg.

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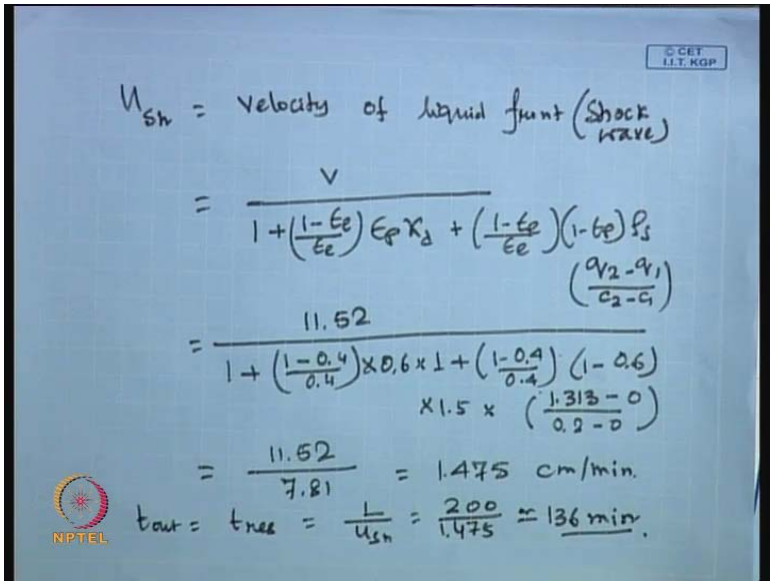


Now, you are in a position to get the velocity of the shock wave. This is the velocity of liquid front, which is nothing but we are terming it as a shock wave. This will be velocity. This velocity will be interstitial velocity divided by 1 plus 1 minus epsilon e divided by epsilon e into epsilon p k d, plus 1 minus epsilon e divided by epsilon e into 1 minus epsilon p, rho s, and delta q by delta c will be in this case nothing but q 2 minus q 1 divided by c 2 minus c 1. This interstitial velocity was 11.52. Now, put the different values of different parameters. This becomes 11.521 plus epsilon is 0.4. So, 1 minus 0.4 divided by 0.4, epsilon p is 0.6, it is given. So, it is 0.6, k d value is 1, plus 1 minus

epsilon e which is 0.4 divided by 0.4, into 1 minus epsilon p. So, 1 minus 0.6 and rho s is given as 1.5.

So, it will be multiplied by 1.5 into q 2 minus q 1, q 2 is the saturation point; that means, q 2 is the corresponding to value of the concentration c 2 that we have already found out. It is 1.313, and what is q 1? q 1 is the value when you started the operation. So, it is a step change basically. Initially, there was nothing and now you have suddenly the saturation point. So, q one will be 0, and c 2 you are having 0.2 molar and initially there was nothing in the column. So, if you put everything in, if you just simplify the denominator, it turns out to be 7.81 and the velocity it turns out to be 1.475 centimeter per minute. So, t out, which is same as t residence time, is nothing but length l divided by the shock wave. In this case, the length is 2 meter. So, 200 centimeter, 200 divided by the velocity is 1.475 and it turns out to be around 136 minute.

So, there is the residence time for this particular solute when it is coming out of the column. Now, if you have another solute in addition to these solutes. So, what you will be having is that from that second solute, the adsorption isotherm will be different. So, this term, on the third term (Refer Slide Time: 17:42) on the denominator to the extreme right hand side, this term will be different for the second solute.

So, that will give you a different value of the shock wave velocity for the corresponding second solute. So, the residence time will be the different for those particular solutes. Suppose, the residence time you calculate is a 150 minute, that simply means at 136 minutes, you will be getting a peak for component A, at 150 minutes you will be getting a peak for component B. So, that is how these things work and that is a principle of operation of chromatographic column.

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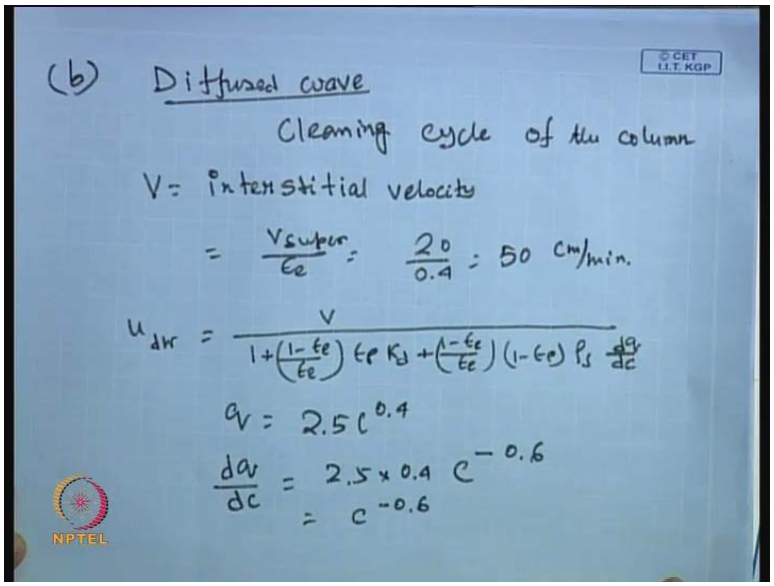


Let us talk about the part two. So, that goes for the part a. Part b is the diffused wave and this is the cleaning cycle, cleaning cycle of the column. In this case, the interstitial velocity will be different, because the superficial velocity is different. 20 divided by 0.4, this turns out to be 50 centimeter per minute. Then the u, velocity for the diffused wave turns out to be same thing. You use the same formula; v by 1 plus 1 minus epsilon e by epsilon e into epsilon p times k d, plus 1 minus epsilon e divided by epsilon e into 1 minus epsilon p, rho s times delta q by delta c.

This time in this case it will be d q by d c, because there is a gradual change of q with respective c in diffuse wave. The earlier case it was a shock wave, so that the delta q was, it was shock, so it was represented by delta q by delta c. Now, since it will be the delta c will be basically tending to 0, so it will be very small velocity of delta c. You will be getting a change in delta q, so it will be d q d c. So, q is given as 2.5 c to the power point four. So, if you differentiate with respect to c, d q d c turns out to be 0.4 will be coming outside. So, 2.5 into 0.4 divided by c and minus 1. So, it will be minus 0.6. So, it will be basically c to the power of minus 0.6.

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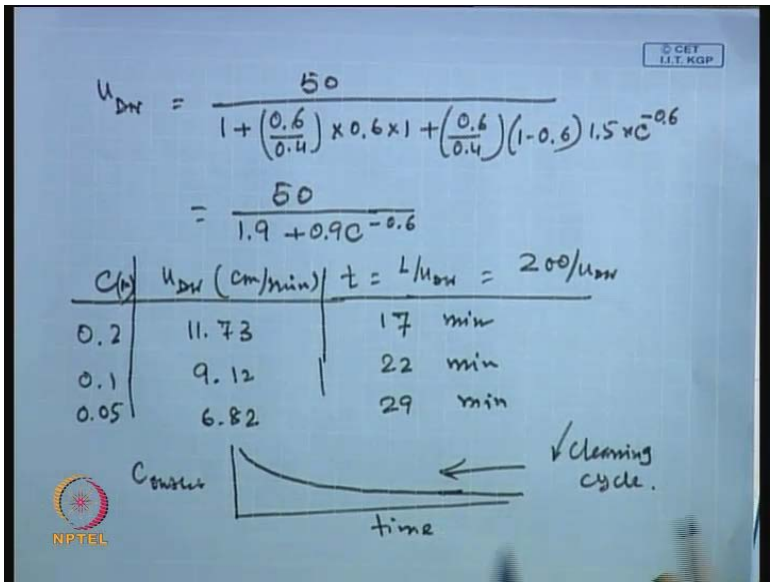


So, now, you put all these values in your diffused wave velocity. This turns out to be 50, which is the interstitial velocity in the particular case. 1 plus 0.6 divided by 0.4 into 0.6, into 1 plus 0.6 divided by 0.4, into 1 minus 0.6, that is 1 minus epsilon p, rho s is 1.5 and d q d c, I will be replacing it by c raise to the power minus 0.6. If you just simplify this equation, this turns out to be 50 divided by 1.9 plus 0 .9 c to the power minus 0.6.

Now, for different values of c, at the outlet, you will be getting different values of different residence time. So, c versus time will be looking something like this. C is in molar concentration and u s, u d v, will be in centimeter per minute. You can prepare this table and this time will be nothing but, l by u d w. So, it will be two hundred divided by u d w. So, for 0.2, if you calculate u d w it turns out to be 11.73 centimeter per minute and if you calculate the residence time, these turns out to 17 minute.

Similarly, for 0.1, you will be getting 9.21 and it will be 22 minute. If you go further less like 0.05, it turns out to be 6.82, and these will be 29 minute. So, if you plot c of the solute at the outlet versus time, initially, you are going to get a very high value. For a small value of time you will be getting high value. So, the profile looks something like this. So, it will be decreasing. So, this is the cleaning cycle. In fact, you can go for the very low concentration and concentration of c and can evaluate what is the time. So, you can find out what is the cleaning time cycle should be required to clean this column up. Once this column will be cleaned, this column is ready for injection to, for analysis of

another a fixed solution continuing different kinds of you know, either a mixture of solute or a particular component. That is how the calculation for chromatography column will be done.

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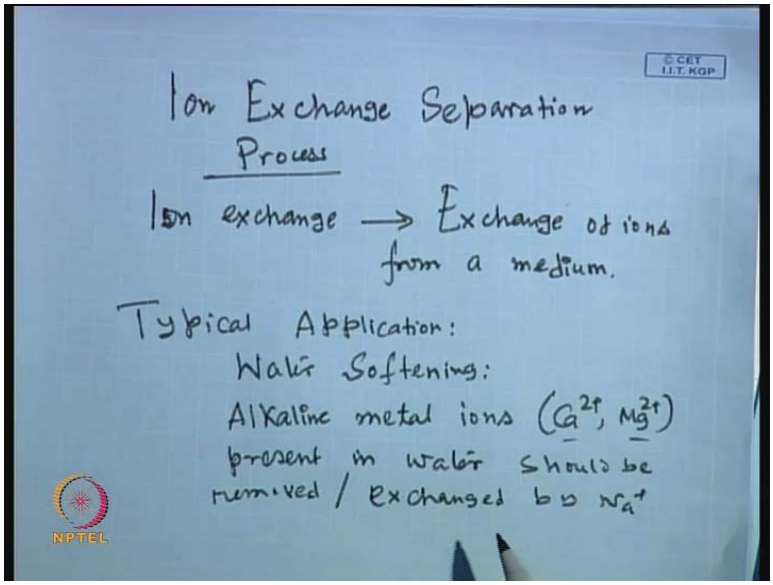


And next we will move to the next separation process that is the Ion Exchange Separation Process. This ion exchange simply means exchange of ions in a medium. It has a typical application in water softening; its typical application is water softening. What do you mean by water softening? In water you will be having the alkaline metals like calcium, magnesium and things like that. So, alkaline metals, metal ions present in water should be removed or exchanged by Na plus. So, we like to remove the calcium, magnesium and in favor of Na plus. So, sodium will be coming from the solid phase to the liquid phase, on the other hand calcium, magnesium etcetera will be going from the liquid phase to the solid phase and you will be getting fixed on the solid phase. So, the liquid that is coming out of the column will be devoid of alkaline metals.

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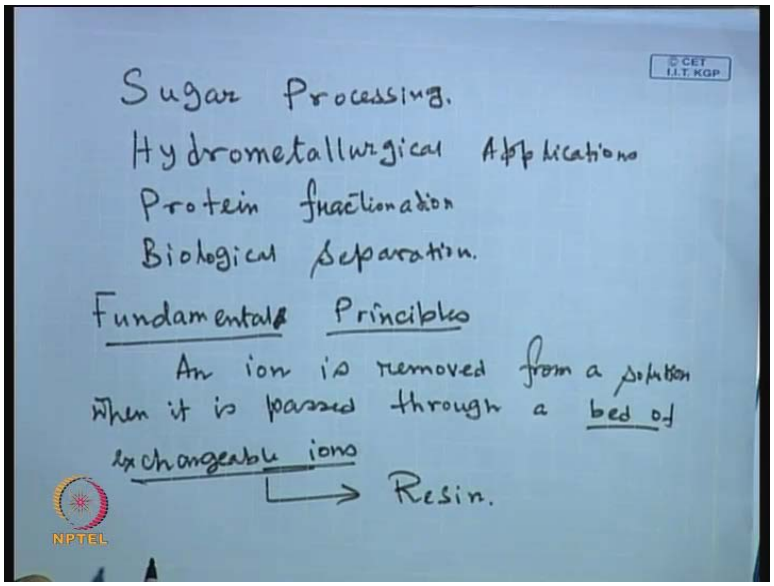


So, that is the water softening application. Then it can be used for sugar processing, it can be used for hydrometallurgical application and it can be used for protein fractionation. Suppose, you have a column, which is specific to a particular protein from a mixture, so that protein will go from the liquid stream to the solid stream, so the protein will be fractionated and biological separation, so on and so forth.

So, let us look into the fundamentals; fundamental principles of ion exchange method. So, an ion and undesired ion is removed from a solution when the solution is passed through a bed of exchangeable ions. The bed of exchangeable ions is called a resin. The bed of exchangeable ion is called a resin.

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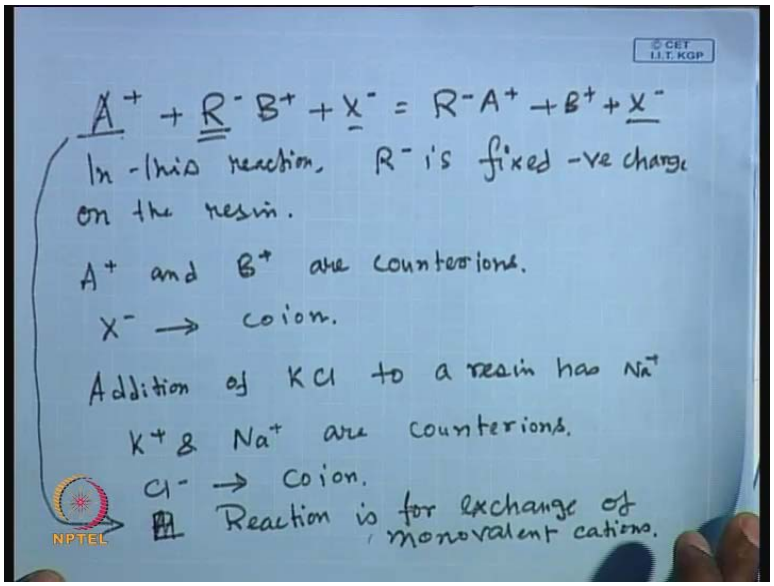


And that typical reaction that you will encounter in the ion exchange resin is A plus, plus R minus B plus, plus x minus will be is equal to R minus A plus, plus, B plus, plus x minus. So, in the resin, in this reaction R minus B plus is the resin, and R minus is fixed negative charge on the resin. A plus and B plus are counter ions; that means, A plus is present in the liquid stream, B plus is present in the solid state and A plus will be displacing the B plus and it will be exchanged and A plus will be fixed in the solid state and B plus will be coming to the liquid stream. X minus is the co-ions that is coming through the liquid steam because electro neutrality would be always maintained.

CaCl2, for example, if you have a solution, which will be having a calcium ion, so whenever the calcium ion is present or magnesium ion will be present, the co-ions also, means counter ions will always be present. Calcium and chloride, the calcium and magnesium, they will be always associated with the negative ions, either they will be chloride ions or they will be sulfate ions. It will be in the form of magnesium sulfate or calcium sulfate or calcium chloride, magnesium chloride in that form. So, there will be, so that the solution will be electro neutral always. X minus is the particular co-ion.

Example is, addition of K C L, let us say addition of K C L to a resin, which has N a plus ions. So, here K plus and N a plus are counter ions with respect to the R minus present in the resin, and Cl minus is the co-ion. Now, these reaction that we have shown is

exchange of monovalent counter ions. This reaction scheme is for exchange of monovalent cations. Let us say. So, similarly, the ion exchange process will be done.

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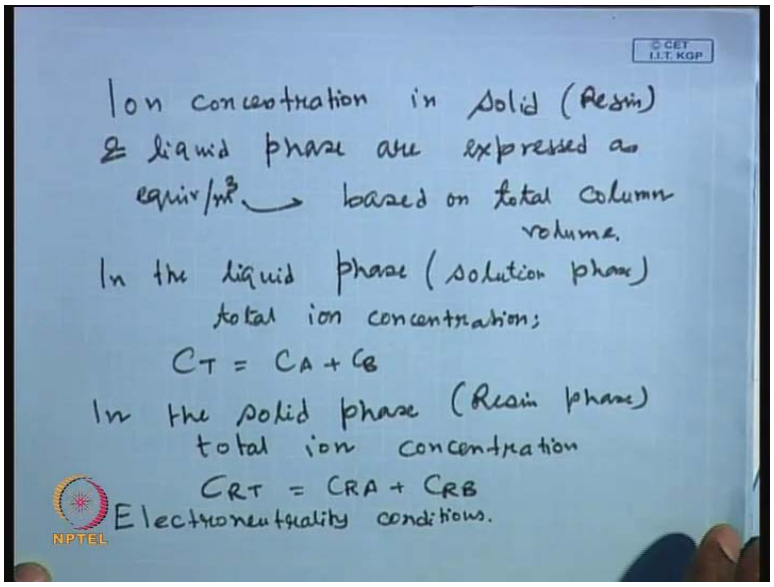


Now, the ion concentration in solid phase; solid phase means the resin phase, liquid phase means the solution phase. In the solid phase and liquid phase are expressed as equivalent per meter cube, not molar per meter cube. It will be equivalent per meter cube and this is based on total column volume. So, in the solution, in the liquid phase or the solution phase the total ion concentration is fixed. So, C T, C total is equal to C a plus C b. In the solid phase or the resin phase, the total ion concentration can similarly, be written as C Rt is equal to C RA plus C RB. The subscript R indicates that it is in the solid phase of the resin phase. These two conditions are known as electroneutrality conditions. So, if one total is constant means if one ion will be increased, the corresponding part of the counter ions also is increased to make the total constant. So, this electroneutrality condition will be holding for the both the phases.

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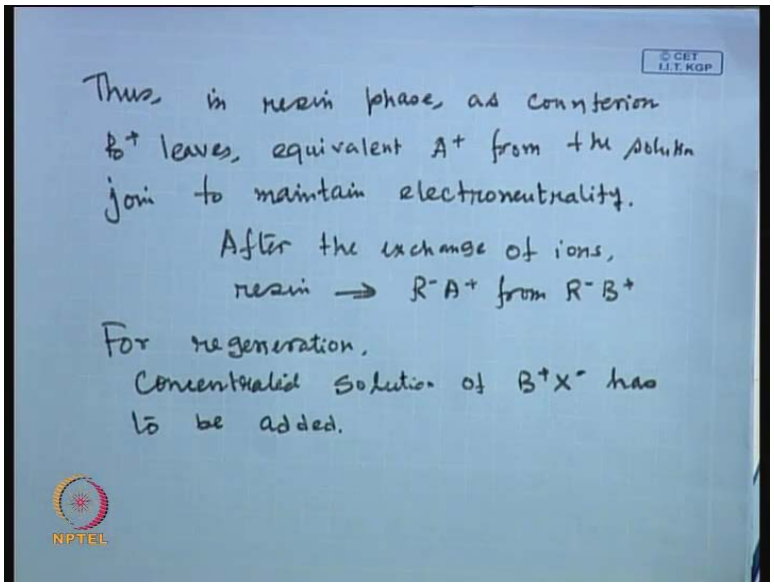


Thus in Resin phase as counter ion B plus leaves equivalent A plus, from the solution join to maintain electroneutrality. So, after the exchange of ions, resin gets transformed from R minus A plus to R minus B plus and to generate the resin for regeneration, concentration solution of B plus X minus has to be added to the column.

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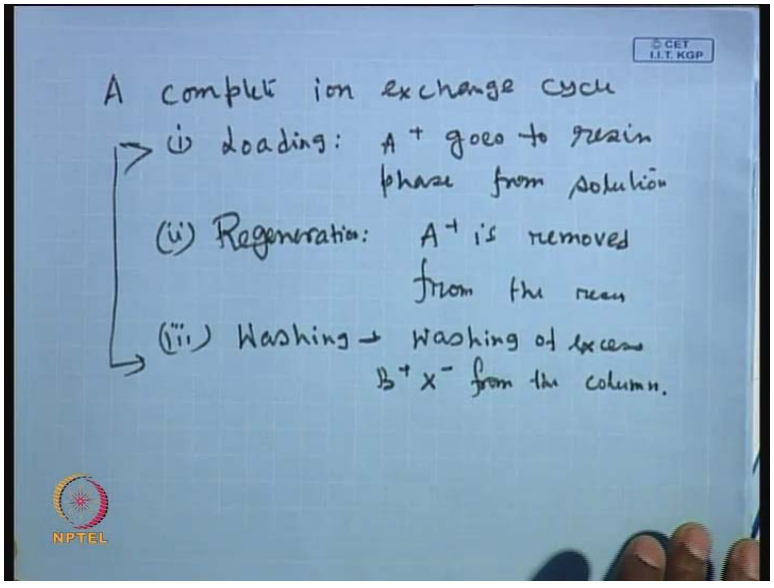


So, a complete ion exchange cycle consists of three steps. Complete ion exchange cycle has three distinct steps; number one is called loading. What is loading? Loading is A plus goes to resin phase from solution, second one is regeneration, A plus is removed from

the resin and third one is called washing. Washing means washing of excess B plus X minus from the column. So, that gives the complete cycle of an ion exchange resin column. Now, in the reaction that we have talked earlier that represents when monovalent ion is being exchanged, but most of the water (( )) the divalent calcium or magnesium would be exchanged, so that the reaction would be different.

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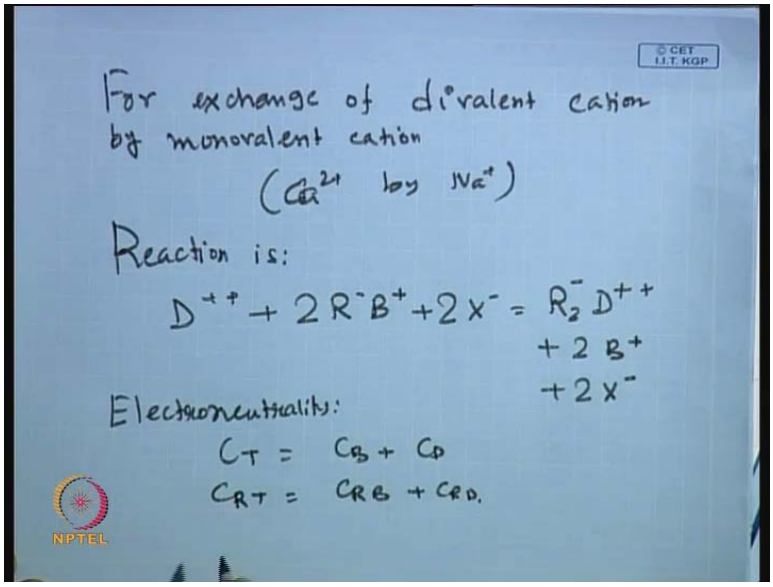


For the exchange of divalent cations by monovalent cations; that means, divalent cation is present in the liquid phase and monovalent caption present in the solid phase; that means, I am talking about exchange of Ca 2 plus from the solution by Na plus, present in the resin phase. So, therefore, the electroneutrality condition, the reaction is D plus plus, plus 2 R minus B plus, plus 2 x minus will be equal to R 2 minus D plus plus, plus 2 B plus, plus 2 X minus. So, divalent ion occupies two sides of the resin. Now, electroneutrality conditions will be maintained both in the solution phase as well as in the resin phase. So, C T will be is equal to C B plus C D in the liquid phase and in the resin phase it will be C RB plus C RD. So, once the concentrations of different species will be known then you can find out the mole fraction of various species.

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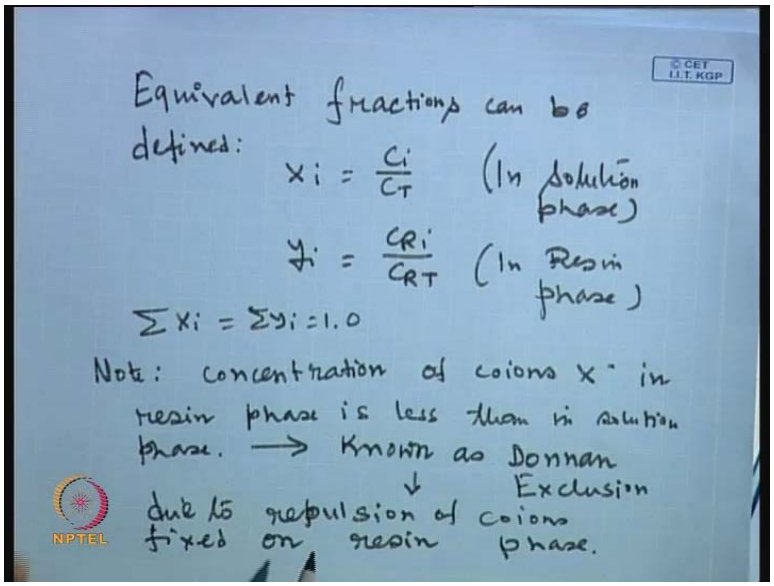


So, the equivalent fraction, because the concentrations are now we expressed in equivalent per meter cube, so equivalent fraction can be defined and these are x i is equal to c i by c t, which is a mole fraction of component i, in the liquid phase. So, these in the solution phase. In resin phase you will be having y i is equal to C R i divided by C R t, in resin of the solid phase. Please note that summation of x i is equal to summation of y i will be always equal to 1, mole fraction of all of them will be equal to 1.

Also to be noted that the concentration of co-ions like X minus in resin phase is less than in solution. These particular phenomena is known as the Donnan exclusion, this phenomena is known as Donnan exclusion and these occurs because the repulsion of the co-ions in the resin phase due to repulsion of co-ions fixed on resin phase.

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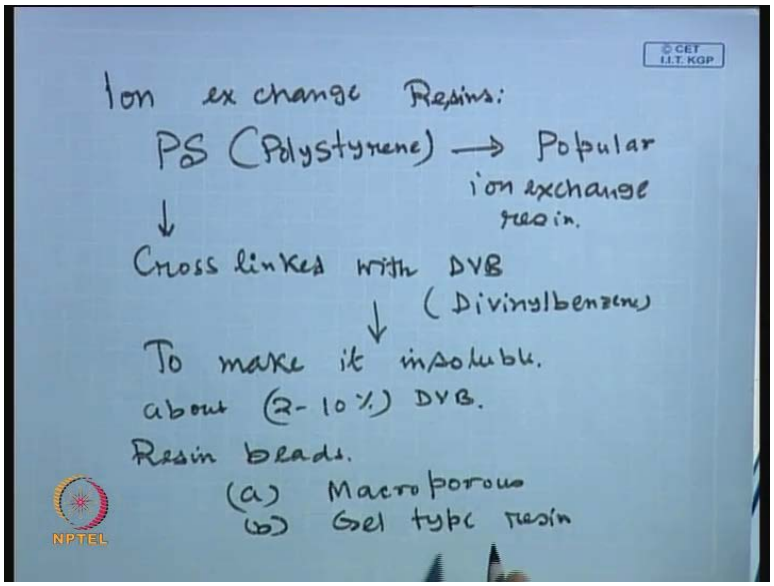


Let us look in to the various types of resins, ion exchange resins. Most popular ion exchange resin is polystyrene known as P S is the popular ion exchange resin. It is cross linked with divinylbenzene, with DVB, that is called divinylbenzene, to make it insoluble in aqua stream. About 2 to 10 percent of DVB is used for cross linking. There are 2 types of resin beads are used. Resins are generally in the form of beads. One is macroporous, another is gel type resins. Macroporous are solid beads with lots of pores inside it and gel type beads are almost are viscous type of material. This on the transition of the liquid as well as the solid, highly viscous material

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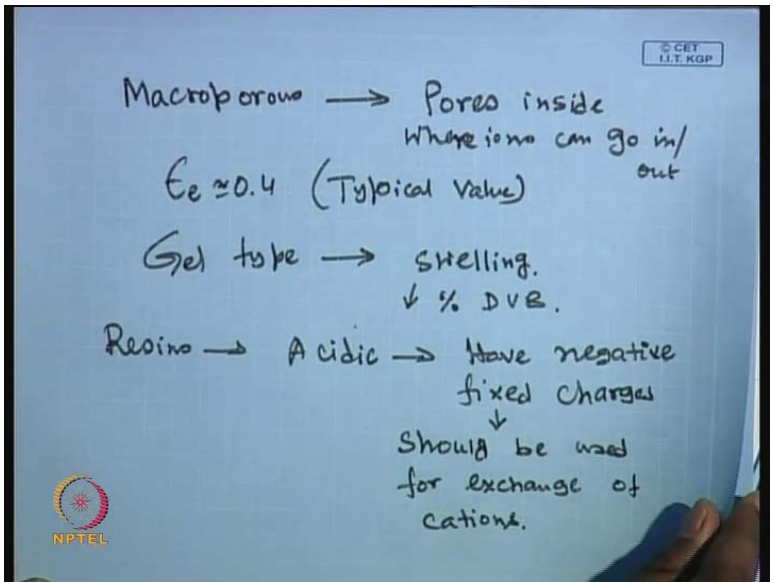

So, macroporous beads, they have the pores inside, where ions can go in or they can go out. So, ion can have a moment through them. Typical external porosity is about 0.4. Epsilon e is about 0.4, there is a typical value. The value of the macroporous beads and gel type resin has different degrees of swelling. Gel type, they have the typical property of swelling. One the other hand, the macroporous beads, they do not swell, they are almost solid particles. On the other hand Gel type, they will swell when they absorb water and they have the various degrees of swelling and it will be depending on percentage of cross linking by DVB.

Now, there are two type of resins generally; acidic resins and basic resins. The acidic resins have negative fix charges and they can exchange cations, have negative fixed charges. If they have negative fix charges they can be used for the cations, should be used for exchange of cations only.

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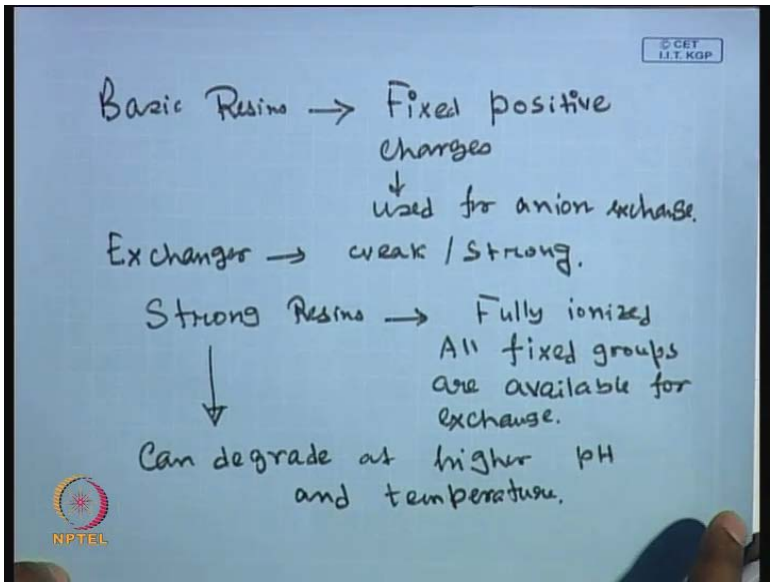


On the other hand, the basic resins they have fixed positive charges used for anion exchange. Now, these exchanges can also be weak and strong. It can be weak or they can be strong. Strong resins are generally fully ionized and all fixed groups are available for exchanging, available for exchange. On the other hand, the strong resins can degrade at higher PH and temperature. That is also disadvantage. They can be degraded because they are fully ionized, they can degrade at extreme PH conditions that is higher PH and temperature.

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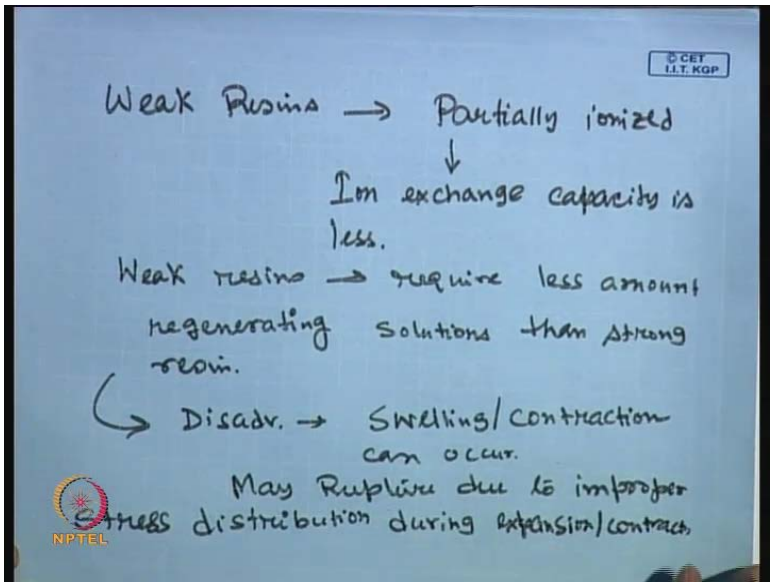


On the other hand, the weak resins are partially ionized. Since, they are partially ionized their ion exchange capability will be less and weak resins require less regenerant than strong resins and that is true. Since, they are weak resins, they require less amount of regenerating solution. So, in case of strong resins, the ions that are fixed on the solid phase, is difficult to move them out. So, you require huge amount of regenerant. On the other hand, in case of weak resins, you will require a less amount of regenerant for obvious reasons.

On the other hand the disadvantages of the weak resins are that the resins will swell or contract when ions are exchanged. Swelling or contraction can occur and they can even rupture due to improper stress distribution during expansion or contraction cycle. It may rupture due to improper stress distribution; during expansion or contraction cycle. Also in case of weak resin the ions diffuse slowly.

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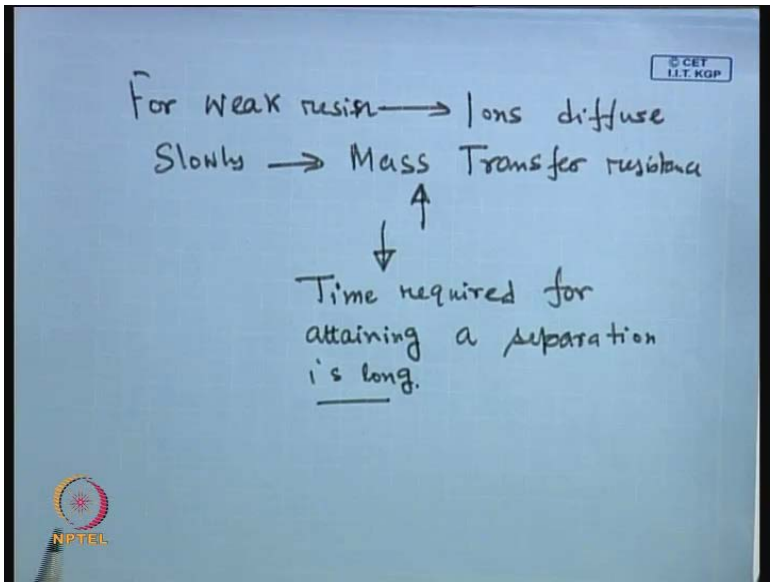


When the ions diffuse slowly then the mass transfer resistance will be extremely high. So, since the diffusion is very slow, the mass transfer resistance is remarkably high because the mass transfer resistance is remarkably high, the time required for attaining a separation will be long. So, these are the various advantages and disadvantages of weak and strong resins, acidic resins and basic resins.

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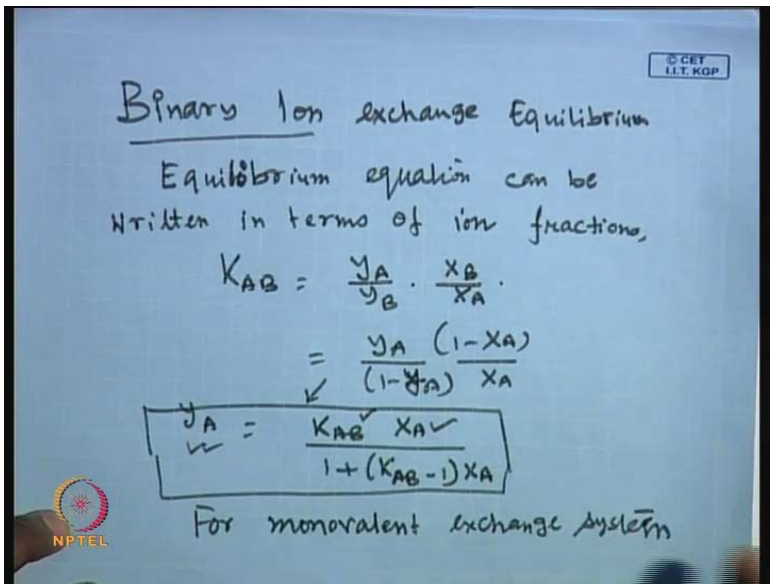


Now, let us look into the binary ion exchange equilibrium. By now, it must be cleared to you that the ion exchange is a process is an equilibrium governed separation process.

Unlike the membrane processes, which are rate governed separation processes, so it will be entirely governed, by the equilibrium of the ions, present in the solid phase and the liquid-phase. It cannot achieve a separation, which is beyond the equilibrium composition. So, equilibrium equation can be written in terms of ion fractions K A B, is equal y A by y B multiplied by x B by x A, and you can change the x B and y B in favor of y A of component A, by simply one minus x A. This is one minus y A multiplied by x A. So, y A can be and you can extract y A from this equation.

You can get y A in terms of x A that is |K A B x A divided by 1 plus K A B minus 1 times X A. So, from this equilibrium relationship, if you know the equilibrium constant K A B and if you know the liquid phase concentration or liquid phase composition, you can find out what is the solute composition in the solid phase. This equation is for monovalent echange system.

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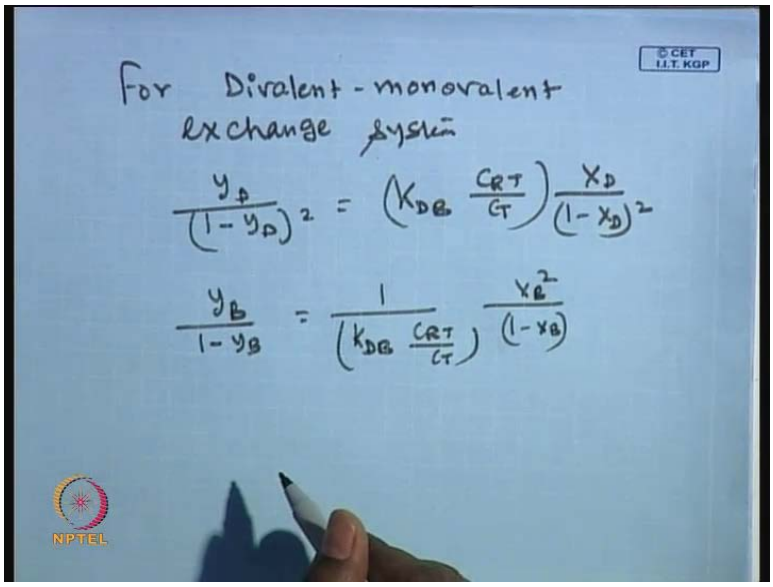


In case of divalent-monovalent exchange, so the earlier cases were for monovalent-monovalent; that means, two ions which are of valency one they will be exchanged. For divalent-monovalent exchange system which is of primary interest to us, which means calcium or magnesium will be exchanged in by sodium plus. It will be y D divided by one minus y D square is equal to K D B multiplied by C RT divided by C T. K DB is a constant, equilibrium constant C RT is basically the total concentration in the resin phase, solid phase, and C T is the total concentration in the liquid phase, and y D is the

mole fraction of the divalent cation, multiplied by x D divide by 1 minus x D square. You can have y B divided by 1 minus y B is equal to one over K DB into C RT divided by CT, whole into x B square divided by 1 minus x B.

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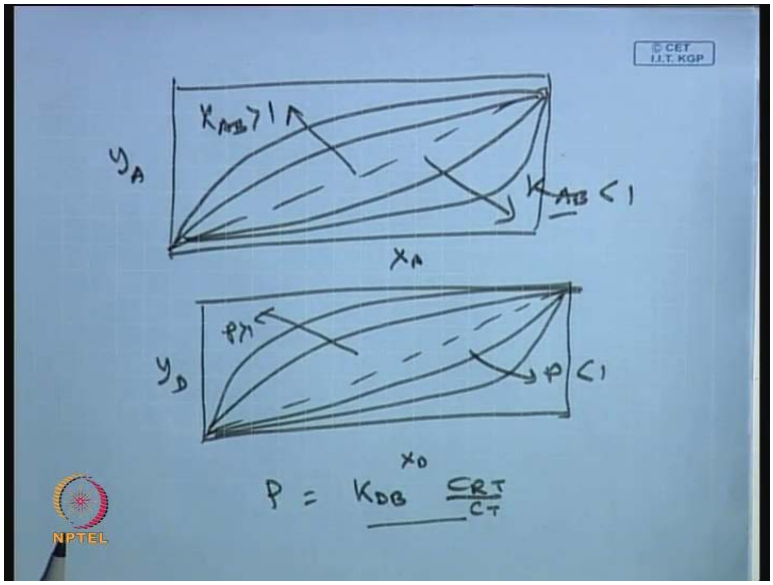


Now, using this equilibrium, if you into the equilibrium curve, the equilibrium curves will look something like this. Now, if you plot the y A versus x A, these let say 45 degree line, will be getting curves like this. On the other hand, you will be getting curves like this. This will be K AB, is much greater than one and this side it will be K AB is much less than one.

For the divalent monovalent exchange system, you will be getting y D versus x D. So, here P is greater than one and in this case P is less than one. What is P? P is nothing, but, K DB multiplied by CRT by CT, so depending on this parameter, the equilibrium constants, so you will be getting curve either concave up or concave down. Now, using the equilibrium curves, one can really go for the ion movement theory, and find out and evaluate what is the ion velocity in the ion exchange resin. Once you know the ion velocity in the ion exchange resin then exactly like the column chromatography column calculations, we can really do the calculations and find out what is the total residence time and what is the total regeneration time, what is the total washing time and what is the cycle time .

So, in the next class what we are going to do is we will explain the ion movement theory and we solve one particular example to calculate the total time that you will be requiring for a total full ion exchange resin cycle.

Thank you.