Chemical Reaction Engineering II
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Lecture - 20
Gas - liquid reactions - 1: Theories of mass transfer into agitated liquids

My name is A.K. Suresh and I am from the department of Chemical Engineering at IIT Bombay. In the next few lectures, I will be talking about an important class of heterogeneous reactions namely: Gas liquid reactions. Now, these are important from an industrial point of view as well as an academic point of view. From an industrial point of view because, industry uses these reactions for 2 important objectives; one is to do a gas cleanup.

For example: removal of carbon dioxide from flue gases and removal of catalyst poisons such as h 2 s etcetera or carbon monoxide from gas streams, which are to be subjected to any further reactions steps. And the second objective is to make products of commercial value such as for example of absorption of sulphuric oxide in sulfuric acid to produce oleum, absorptions of nitrogen oxides in water to produce nitric acid and so on. They are important from an academic point of view, because there are more complex 3 phase's systems or even more complex multi phase systems who analysis runs in a similar manner to the analysis gas liquid reactions.

Let us, provide some contexts. So, you can see where, this class of reactions fix into the general landscape of reactions engineering that you have been seeing so far. When we study reactions, we usually begin with the simplex class of reactions which is homogeneous reactions. Now, these are reactions in which everything is in the same phase, all the reactants and products and catalysts. If there are some, they are all in the same phase and the reaction expressions turn out to be simple. They are often of the type you know c a raised to m and c b raised to n type of rate expressions.

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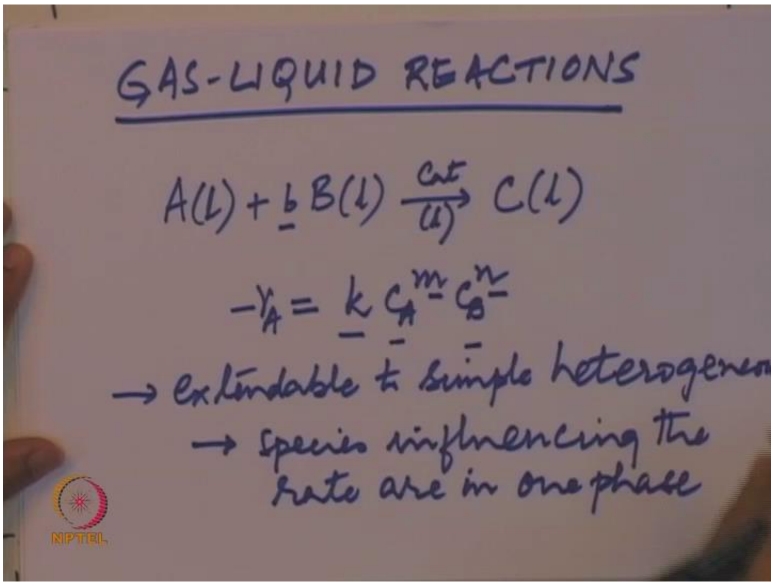

GAS-LIQUID REACTIONS

$$A(l) + \underline{b}\,B(l) \xrightarrow[(l)]{cat} C(l)$$

$$-r_A = \underline{k}\,\underline{C_A}^{\underline{m}}\,\underline{C_B}^{\underline{n}}$$

→ extendable to simple heterogene

→ species influencing the rate are in one phase

Let us take an example such as reactions A in the liquid phase reacting, with B in the liquid phase; lower case b being the stoichiometric factor giving C also in the liquid phase. So, this is the liquid phase reaction, because the reactants as well as the product and if there is a catalysts the catalysts as well are all present in the liquid phase. Now, such reactions we have seen before and they are often analyzed using expressions of this type.

The analysis is simple, the experiments to recover the values k, m and n are straight forward to set up and interpret. And the design of reactions using these kinds of rate expressions is also relatively straight forward. Now, the method of analysis that we use for these kind of reactions can also be extended to simple heterogynous systems, as long as the species influencing the rate are in 1 phase.

So, what I am saying is in this reaction for example: the rate expression contains the concentration of A and the concentration of B and as long as the ads A and B is present in the same phase. It does not really matter whether C is in the same phase or not, it might volatiles volatile product or it might precipitate out of the phase. But, the method of analysis is essentially the same as if C was also in the same phase. However, the matter gets somewhat complicated when the reactants and catalysis's, if there is 1 are distributed among different phases the simplest of… So, these are what are heterogeneous reactions as you know and the simplest of these reactions.

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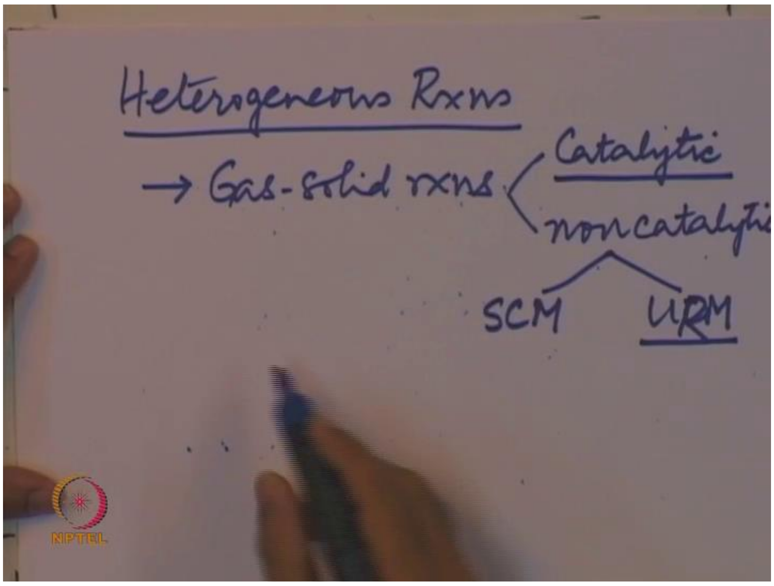

So, let say heterogeneous reactions and simplest of these are those in which there is a continuous phase and there is disperse phase and there are just 2 phases. Now, we have already seen 1 class of such reactions, which are gas solid reactions and in gas solid reactions you have seen 2 types. One is catalytic, in which case you model diffusion in the porous of the solid catalyst. And you recover a concentration profile of the diffusing reactant and use that to construct what is known as an effectiveness factor, which has the factor that modifies the intrinsic rate.

On the other hand you have also studied non catalytic gas solid reactions. Which further can be grouped into models in or situations in, which the reaction takes place at a front and this leads to the shrinking core type of models. And you have also seen reactions in which the reaction takes place throughout the solid and these are these reactions are described by what are called as Uniform Reaction Model, Uniform Concentration Models.

In the catalytic reactions as well as the Uniform Reaction Models will call this URM Uniform Reaction Models. As I said earlier, you are modeling the concentration profile through the solid and for simplicity you can create the solid particles to be spherical in shape. And then you write the diffusion equation for a sphere. Get the concentration profile diffusion with reaction get the concentration profile. And differentiate the concentration profile at the surface to find out the rate at which the reactant is entering into the solid, which is the rate at which the reactant is being consumed by reaction.

Now, whether it is catalytic, whether it is non catalytic, whether it is shrinking core, whether it is uniform reaction the point to be noted is that the reactions are in the dispersed phase.

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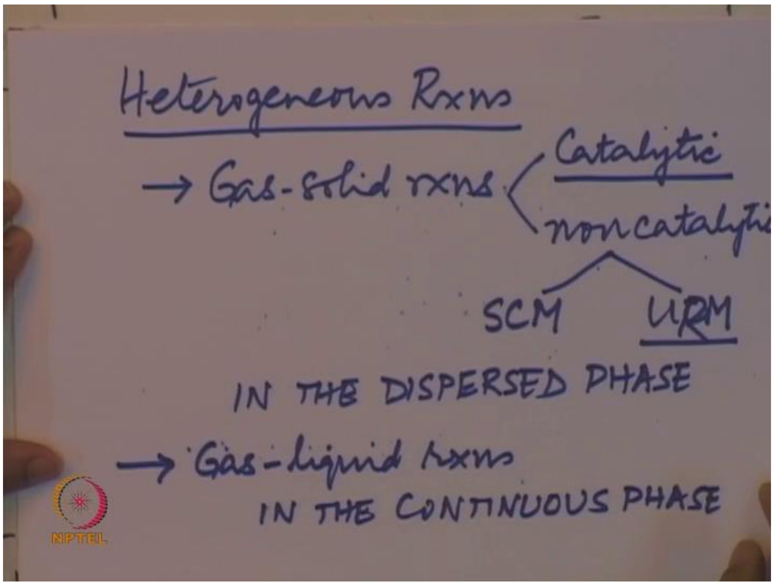

Heterogeneous Rxns

→ Gas-solid rxns < Catalytic / non catalyti

SCM URM

IN THE DISPERSED PHASE

→ Gas-liquid rxns

IN THE CONTINUOUS PHASE

The reactions are in the dispersed phase which happens to be solid in this particular case. By contrast the type of reactions that we are going to study now, which are gas liquid reactions are those in which the reaction is the continuous phase. This is because the normal situation with gas liquid systems is, for example: a gas being bubbled through a column of liquid, which may be being stirred as in a purged in a stirred reactor or which may be being stirred by the flow of the gas itself, such as in a bubble column also there are equipments such as packed be D and so on, where also where you can say that there both the gas phase and the liquid phase are continuous.

But, the point is that the reaction is in the continuous phase, which is the liquid phase. So, here the although the although conceptually is shows the very similar to the case of gas solid reactions, the method of analysis has historically evolved in a different way. What is considered for example in the case of gas solid reactions, which I talked about a minute earlier? Is that the reaction is taken as the basic process, there is a certain reaction that takes place at certain intrinsic rate. And the rate of that reaction is modified downwards that is it is decreased by the influence of transport factors by, the fact that the transport is not able to cope up with the velocity of the reaction under all circumstance.

So, there is an effectiveness factor which is which has a value less than 1, which multiplies the intrinsic reaction rate and you get the actual rate of reaction. Where as in the case of the gas liquid reactions, we are going to consider now, what is taken? As a basic process is the process of mass transfer that is, there is gas, there is a liquid, there is a process of mass transfer that can occur weather or not there is a reaction that is taking place. That, if this substance from the gas phase, that is dissolving in the liquid phase has a reactant within the liquid phase to react with. Then the occurrence of the reaction is speed up the rate of mass transfer.

So, there is a basic process of mass transfer, which is speeded up by the occurrence of the chemical reaction. Contrast this with the situation in the heterogeneous catalysis case, where there is a reaction which is slow down by the occurrence of mass transfer or by the existence of mass transfer limitations. So, this is a difference in perceptive that is needs to understood because, here we are going to talk about enhancement factors, which has values more than 1, which multiple the basic mass transfer rate to give you, the rate at which the gaseous salute is being consumed.

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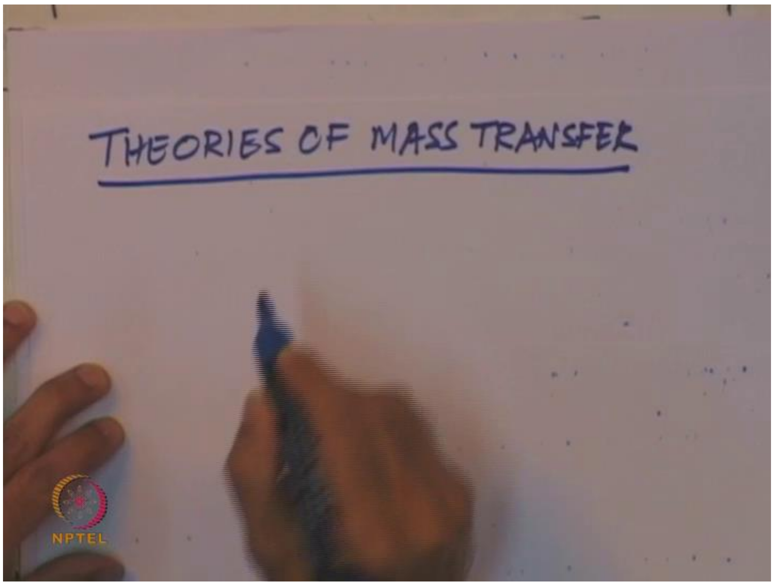

THEORIES OF MASS TRANSFER

So, the basic process being mass transfer, we need to understand the theories of mass transfer, at least we need to revisit the theories of mass transfer. Because these theories provide a mechanistic basis and that mechanistic basis serves as in good stead when we want to include a reaction in the works. So, there are basically 2 theories of mass transfer that we will consider, one of which is called as the Film Theory and the second of which is actually a class of theory, it is not a single theory and that class of theories we will call as the Surface Renewal Theory.

Now, in what I am going to be a talking from a now on I am talking about the processes which are occurring in at any particular location in an equipment like this, for this sake of concreteness.

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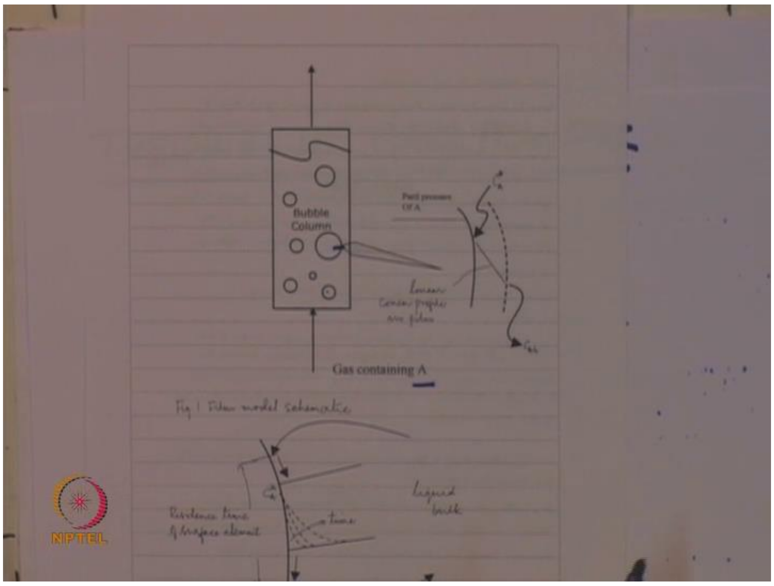

Let us take, bubble column as our equipment now this is a cylindrical such as this and gas is being continuously bubbled through and the liquid may be continuous flow or may be sitting there getting converted it may be batch. So, the gas inside the bubble column exists in the form of bubbles of various sizes, and because of the churning action of the bubbles the liquid is in the state of agitation there is a state of turbulence and what we are talking about is the events that occur at any particular position in the in this kind of an equipment.

For example, say a particular location on the surface of a bubble at which absorption of the gaseous component a is occurring into the liquid ok. So, the gas contains is salute a which is soluble in the liquid and. So, there is no reaction for now. So, the a dissolves in the liquid and diffuses into the liquid that is the process that we are considering. So, the first model that we will consider and additionally, I must also mention that in such a process from your knowledge of mass transfer you know that there is a gas phase resistance and there is a liquid phase resistance in order to keep matter simple.

We will assume that there is no gas phase resistance in the in the initial discussion, we will looked the consequences of including a gas phase resistance towards the end of the this set of lectures.

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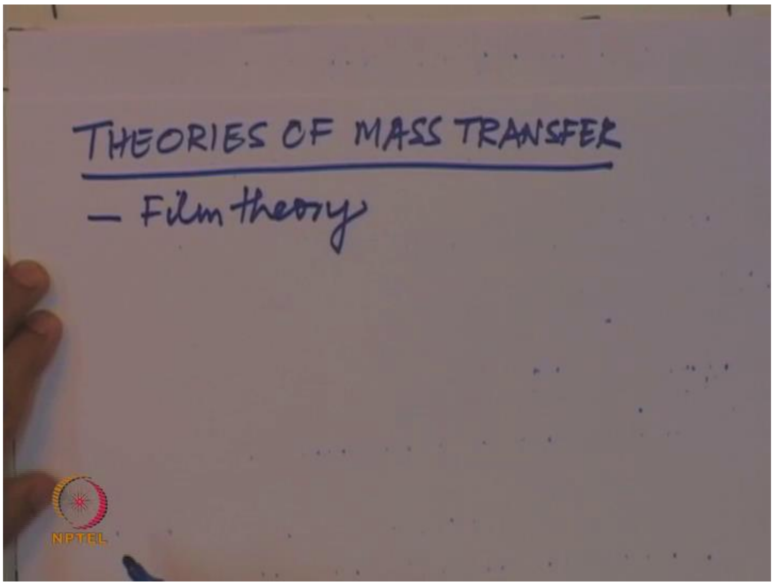

THEORIES OF MASS TRANSFER

– Film theory

So, with those assumptions, now we are ready to consider both types of a visualization which have appeared in the literature the first 1 as I said is called the film theory.

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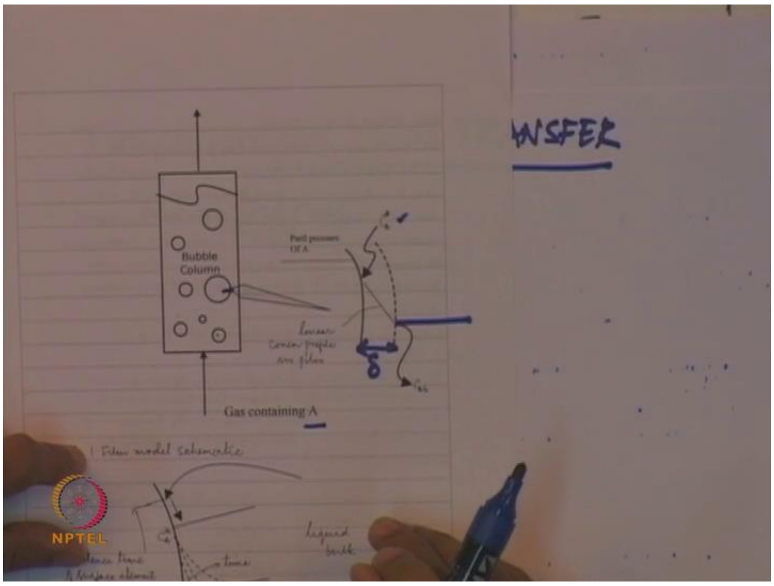

Now, in film theory the situation is assumed to be something like this; this is the gas liquid interface the solid line here, is the gas liquid interface on this side is the gas this is part of the bubble and. On this side is a liquid which is in turbulent motion and what is assumed in the film theory is at the entire resistance to mass transfer is located in a thin film, which is shown by s the region between the solid line and the dash line here.

So, this is called as the film and outside the film the concentration of the salute or concentration of whatever there is in the liquid is assumed to be uniform by the... And it is kept uniform by the action of turbulence there is assumed to be an equilibrium at the gas liquid interface itself in other words the concentration on the liquid side of the interface which I have called asc a star here is in equilibrium with the partial pressure of a on the gas side of the interface, which is assumed to be note because we are assuming that there is no gradients in the partial pressure, there is no mass transfer resistance on the gas side.

So, and this region this thickness of the film is usually denoted by the symbol delta, the Greek symbol delta and it is assumed that there is no turbulence of there is no motion of any kind within this region delta. In other words this film is assumed to be essentially stagnant. And it absorbs the gas by a process of steady state diffusion. Steady state because irrespective of whether, the entire bubble column is operating at steady state or unsteady state the film is always assumed to be in a state of what is called as quasi steady state; what it means is that because the volume of the liquid within the film is so, small the contents of the film get adjusted to any changed to that are happening outside or an instantaneous basis. Therefore, the diffusing species always feels as though conditions are not changing with conditions are study. So, what we have said.

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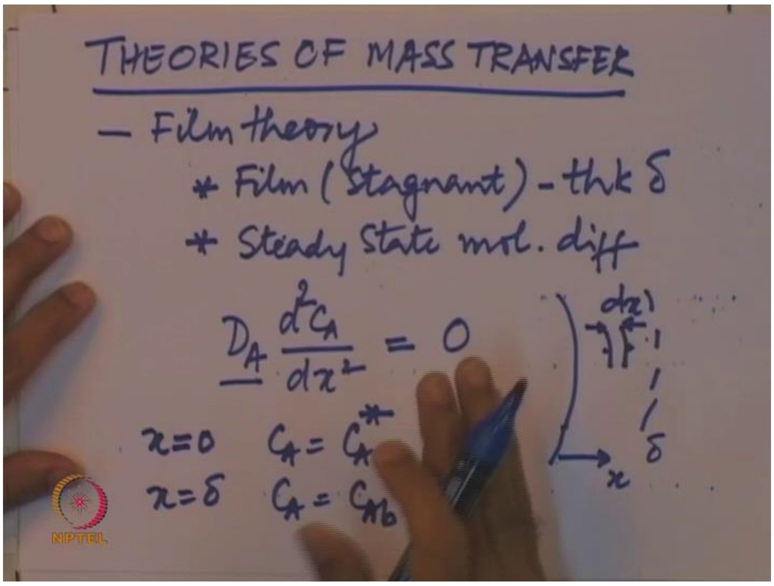

THEORIES OF MASS TRANSFER

– Film theory
  - * Film (Stagnant) – thk δ
  - * Steady State mol. diff

$$D_A \frac{d^2 C_A}{dx^2} = 0$$

$x = 0 \quad C_A = C_A^*$

$x = \delta \quad C_A = C_{Ab}$

So, for is that there is film and the film is stagnant. And the film is of thickness delta and the diffusion process within the film is steady state molecular diffusion, that is because, turbulence cannot penetrate into the film. The effect of turbulence is only felt outside the film in the liquid bulk. So, with these assumptions the governing differential equation is easy to write, you can either make a shell balance as you have done for example, in transport phenomenon, you can refer to the pages on mass transfer Bird Stewart Lightfoot if you need to refresh that that part of the syllabus.

Basically the continuity equation for a is given by DA d squared CA by dx squared equals 0, which basically says that: if you take any you know in the film that I showed of thickness delta, this is the x direction that is the direction away from the gas liquid interface is the x direction. And that is the diffusion is assumed to unidimensional unidirectional. And what we are saying here is that if you take a an infinitesimal element here of thickness dx then whatever is entering at this point must equal the rate at which material is leaving at that point, because there is nothing no accumulation this being steady state. And there is no reaction, therefore there is no consumption.

So, this is the differential equation that describes the transport of a through the film. In this DA is the diffusivity of a through the liquid; these all a through the liquid. Now, this being a second order differential equation requires 2 conditions, 2 boundary conditions in order to formulate it completely. And those conditions are given by saying at x is equal to 0 which is the gas liquid interface, the concentration of A is equal to concentration of A in equilibrium with the partial pressure on the gas side of the gas liquid interface. And A t x equal to delta the concentration of B is equal to CAB, which is the concentration of A in the bulk of the liquid.

So, this is a particularly simple differential equation to solve and what it essentially saying is that: the second derivative of the concentration with respect to x is 0. If the second derivative is 0; the first derivative was be a constant and if the first derivative is a constants the concentration profile is a straight line. So, the solution to this equation is can be shown graphically in this manner.

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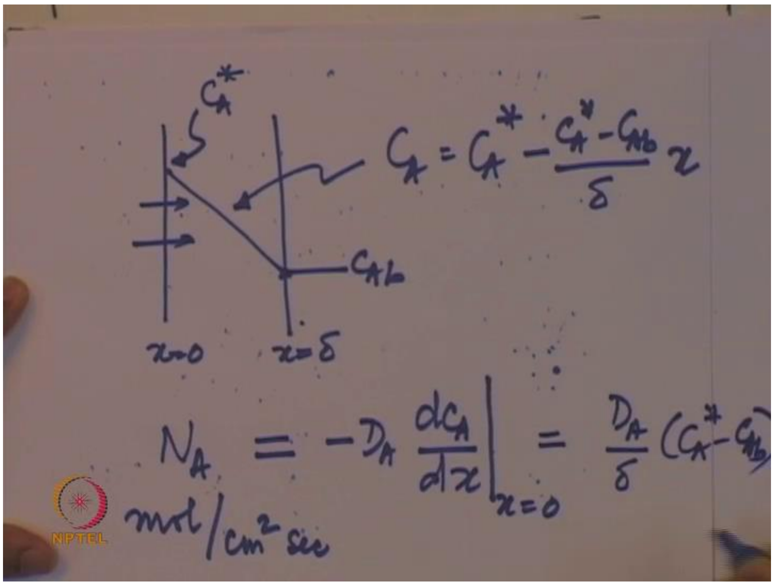

$$C_A = C_A^* - \frac{C_A^* - C_{Ab}}{\delta} x$$

$$N_A = -D_A \left. \frac{dC_A}{dx} \right|_{x=0} = \frac{D_A}{\delta} (C_A^* - C_{Ab})$$

mol/cm^2 sec

So, this is x is equal to 0 this is x is equal to delta and there is a straight line profile that stretches from CA star at the gas liquid interface to CA bulk at the edge of the film. The particular equation that this follows is CA equals CA star minus CA star minus CAB divided by delta multiplied by x you can easily verify that this is a straight line its linear in x. And A t x is equal to 0 this gives CA is equal to CA star, if you put x is equal to delta CA star will cancel and you get CA is equal to CAB.

So, it is satisfies the differential equation it is satisfies 2 boundary conditions. And therefore, this is the solution; what we are interested in is the rate at which gas is entering the liquid. In the gas at the gas liquid interface and that is denoted by NA the flux of A in units of moles of a per unit area, per unit time and this is given by minus DA d CA by dx which is fixed law. So, d CA by dx to be evaluate DA t x is equal to 0 because that is where we want the flux. And d CA by dx is evaluated in a straightforward from the linear equation and we obtained. If you did the simple differentiation you will get this equation coefficient and at driving force.

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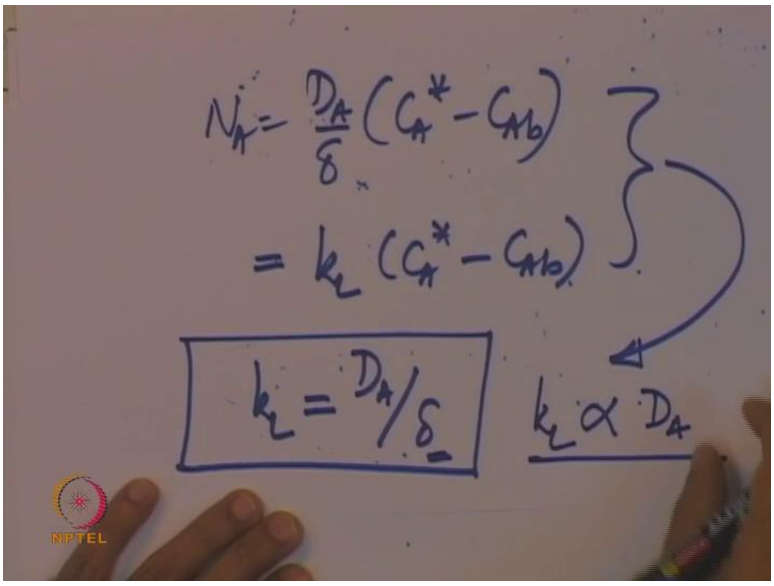

Let me, write that again n a equals DA divided by delta into CA star minus CAB compare this with usual way in which mass transfer into turbulence liquids is described in terms of a mass transfer And comparing these 2, we are arrive at the interpretation of the mass transfer coefficient in the film theory paradime as k l is equal to DA by delta. So, what is this says is that the mass transfer coefficient varies in direct proportion to the diffusivity a in the liquid.

And it varies in inverse proportion to the film thickness. In spite of its appearance this is not in equation that you can use to predict the value of k l, because the value of delta is unknown all you can say is that the stronger the turbulence the more intense turbulence the thinner is the film expected to be, because turbulence can now reach to closer to the interface. Beyond that it very difficult to calculate a value of delta given the conditions of the you know, let us say power input or whatever in the into the liquid.

So, this equation is as much of a definition of k l as it is a definition of delta. So, there is now ay in which you can calculate a value of delta. And therefore, calculate a value of k l this should be taken as saying that the only way to calculate delta is to actually measure the mass transfer coefficient experimentally. And use this equation to calculate delta. So, then what is the use of this equation it makes 1 testable prediction that the mass transfer coefficient is proportional to DA how does this prediction bear out in practice. It turns out that the diffusivity of gases in liquid do not vary over a very wide range. So, it is not the not the most straightforward of matters to actually test this equation rigorously.

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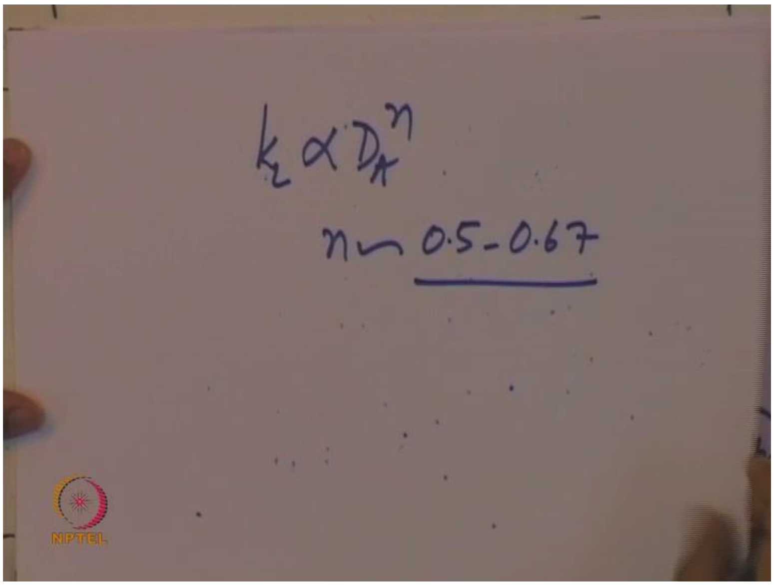

$$k_L \propto D_A^n$$

$$n \sim \underline{0.5 - 0.67}$$

But, available data indicate that k l is actually proportional to DA to the power n, where n has a value that varies between 0.5 and 0.67. In other words it is less than proportional to the value of the diffusivity. So, this is what experiments indicate to the extent that we can make out what the experiments are saying. So, now let us proceeds to the second theory and this as I said is not a single theory.

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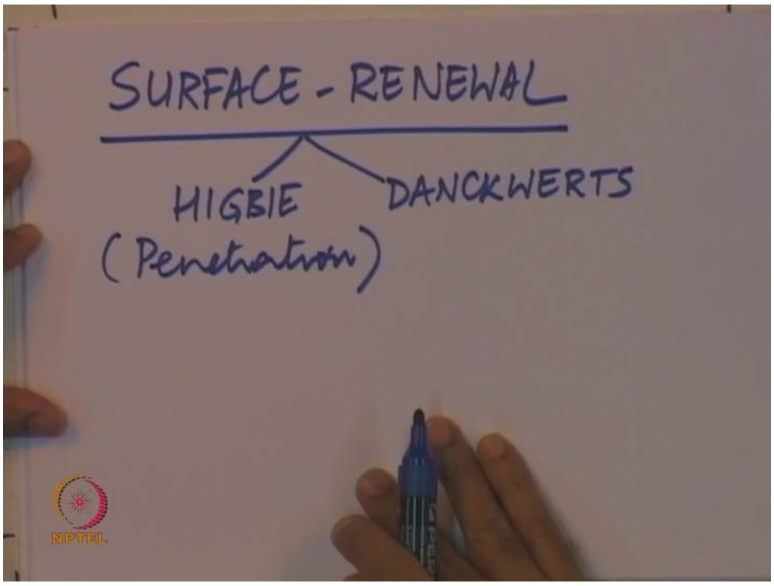

But, this is unknown as we will call this as surface renewal theories. And we will make use of this nomenclature surface renewal to indicate that, the picture of the gas liquid interface in this theory or in this class of theories is 1 of is something that is constantly being renewed. So, material from the bulk of the liquid is constantly being brought to the interface and is constantly being removed from the interface and mixed into the bulk.

So, in this surface renewal theory under this heading of surface renewal theories, we will consider 2 variations 1 due to Higbie and the second due to Danckwerts. The Higbie version of the surface renewal theory is also called as the penetration theory. And Danckwerts version of theory simply called as Danckwerts renewal theory. So, irrespective of whether, we are talking about the Higbie theory or the Danckwerts theory all surface renewal theory I mean there are other versions of the surface renewal theory as well.

But these are the most classical once and it is enough for our propose to really understand these 2 theories, because as we will see later there is no qualitative difference between these theories and various other theories that I have later been proposed. So, irrespective of whether, we are talked about Higbie theory and Danckwerts theory the development is identical up to a point. And it is only at the late stages of theory that, we have to invoke an assumption which will distinguish the Higbie theory from the Danckwerts theory.

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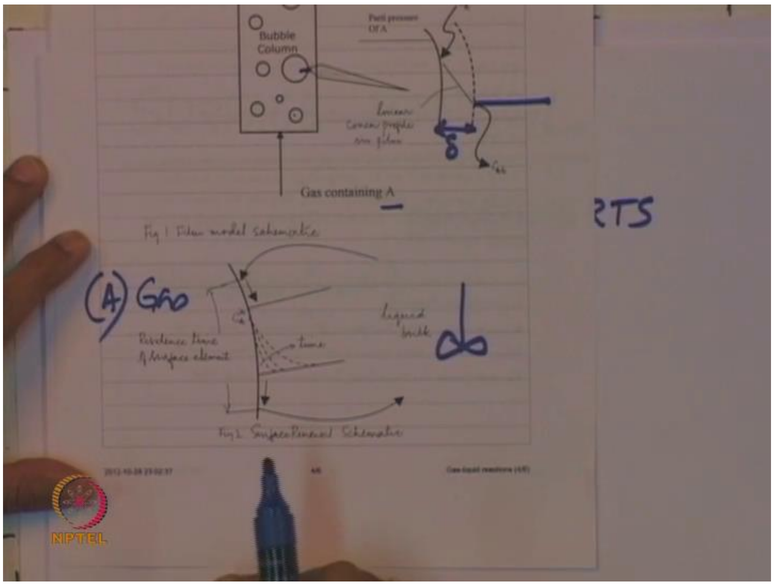

So, let us proceed with a development here what is assumed is that the picture at the gas liquid interface is something like this. So, here this bold line once again is the gas phase liquid interface which is part of the surface of a bubble as we have considered earlier. So, what is assumed here is that the liquid bulk; which is in a state of constant churning because of either agitation or because of gas flow or other means of a creating turbulence and the action of this turbulence is essentially to through elements of liquid on to the surfaces that is what this arrow indicates.

So, elements of liquid from the liquid bulk are thrown on to the liquid gas liquid interface and once there they spend a length of time which we call as residence time of the surface element And A t the end of the time they are removed from the surface. And then recycle to the bulk. While they are residing at the interface they are in direct contact with a surface element is in direct contact with the gas phase salute, which is on this side and the gas phase salute, we have called A and A has a concentration of c a star at the inside the inside the element at the gas phase liquid interface.

In other words what we are saying is that moment, the liquid element lands at the gas liquid interface the interface achieves equilibrium with the gas phase and from there on the salute tries to diffuse into the liquid into the liquid element, for as long as the element is at the surface once the element leaves the surface, it is mixed up with the liquid bulk and the concentrations are even doubt.

So, while the liquid element is at the gas liquid interface what is taking place is a is a process of unsteady state diffusion unsteady state, we came diffusion contrast this with the situation earlier where the processes that we considered, was a steady state k n diffusion process. So, and we are saying that on the microscopic scale at any particular location at the gas liquid interface, the processes an unsteady state p k n diffusion process irrespective of whether the microscopic process in the entire equipment is taking place at a steady state of unsteady state.

This is to be clearly understood because, we are here talking about local rate phenomena only. So, that is what the concentration profiles shown as dash lines here indicate the as time progress as the element spends more and more time at the interface the concentration profiles proceed into liquid in that manner. So, what is the and also another important assumption here, is that the time for which the liquid element resides at the interface is. So, short that the and the penetration of the gaseous salute so, small that the penetration is confine to a region that is close to the interface. So, for all practical purposes the liquid element may be considered to be infinite in depth.

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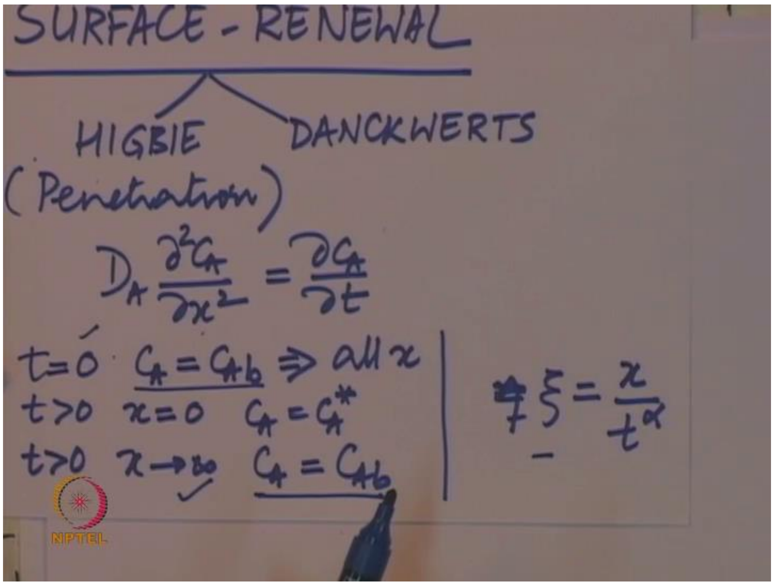

So, what is the governing differential equation then? So, we have to write the unsteady state balance for A and that is shown in that manner. It is a same equation except that the difference in the input minus the output for any differential element is equal to the accumulation here because, we are considering an unsteady state process. So, here x is that direction away from the interface as before. So, this is now a partial differential equation first order in time and second order in x, and therefore we need an initial condition and 2 boundary conditions.

The initial condition is specified by saying that, at t equal to 0. The concentration at the concentration everywhere, within the element is equal to the bulk concentration. So, at time equal to 0 the element has just landed at the gas liquid interface. And throughout the element the concentration is equal to the bulk concentration, which is where t came from at t greater than 0. We have the first boundary condition at x is equal to 0, we have c a equal to c a star in other words what we are saying is that the moment the element arrives at the interface at the gas liquid interface the concentration achieves equilibrium.

At t greater than 0 as x tends to infinity remember that, the element can be considered to be infinitely deep because, the gas does not get to penetrate anywhere near the far end of the element. So, as x tends to infinity the concentration is unchanged, it is the same as what it was at the beginning of the process. So, this is the differential equation and the governing this is governing differential equation and the initial and boundary conditions. Now, you might have seen these kind of equations in our transport phenomena course again either, in a momentum transport or heat transport or mass transport.

These are unable solution by a technique called as similarity transformation; what you notice is that the conditions at t equal to 0 and x equal to infinity are identical at t equal to 0 the concentration is equal to CAB for all x at x equal to infinity for all time the concentration is once again equal to the same value. This suggest that you might be able to define a variable which is a combination of x divided by t to the power alpha; such that the by replacing by doing transformation in terms of this combined variable. We will be able to element t and x completely and have a single ordinary differential equation in terms of xi alone.

So, you can see that the basis for this comes from the fact that this works for an equation of this kind number 1 and number 2 whether x is equal to 0 t equal to 0 or x is equal to infinity xi has the value of infinity And at that value the concentrations are the same. So, the value of alpha which makes this transformation work, can be calculated by substituting this into the differential equation and then find looking for such a value of alpha the. So, that x and t do not occur except as the group of x divided by t to the power alpha, it turns out that the value of alpha that does the job is half.

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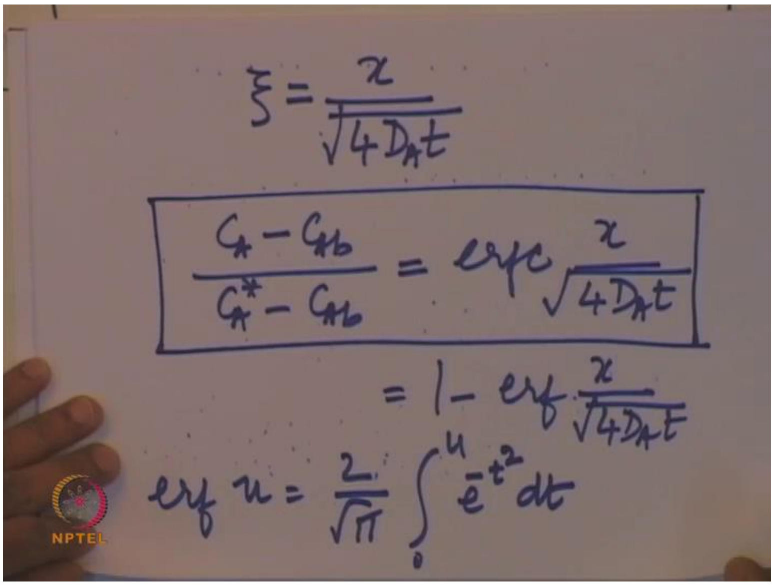

$$\xi = \frac{x}{\sqrt{4D_At}}$$

$$\boxed{\frac{C_A - C_{Ab}}{C_A^* - C_{Ab}} = \text{erfc}\,\frac{x}{\sqrt{4D_At}}}$$

$$= 1 - \text{erf}\,\frac{x}{\sqrt{4D_At}}$$

$$\text{erf}\,u = \frac{2}{\sqrt{\pi}}\int_0^u e^{-t^2}\,dt$$

Or you can deal with a variable of the type x divided by root t. And in order to eliminate some constants what is normally done is this variable is used in order to transform the partial differential equation to an ordinary differential equation. Now, I will not go through the details of the derivation this can be if you substitute this into the differential equation here. It gets transform to an ordinary differentia equation which turns out to be fairly simple to solve. Now, once you have done that you get an equation for concentration which is an error function.

So, it is actually CA minus CA bulk divided by CA star minus CA bulk equals error function compliment of x divided by 4 DA t. This error function compliment is nothing but 1 minus error function of x divided by 4 DA t. And error function itself is define DAs: 2 by root pi 0 to u e to the power minus let us, say t squared d t. So, that is the definition of error function. So, error function is a tabulated function you will find this for various values of u tabulated in mathematical hand books. So, you got this as the concentration profile.

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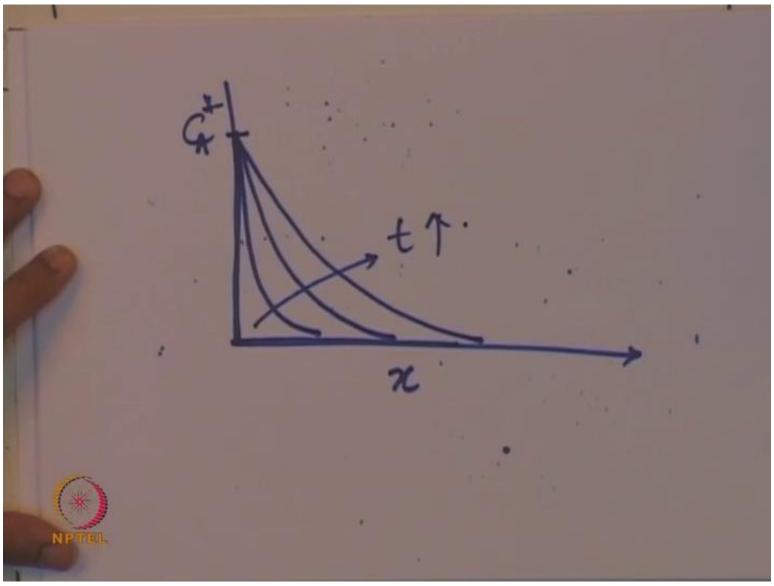

If you plot this concentration profile for various values of time you will get a picture that is something like this. So, you have x And A ll concentration profiles start with CA star as soon as the element lands at the interface it has a profile that is something like this: that is a t equal to 0 at larger values of time you have concentration profiles developing in that manner as t increases. From these concentration profiles, we can calculate the instantaneous rate of absorption in a surface element which has spent.

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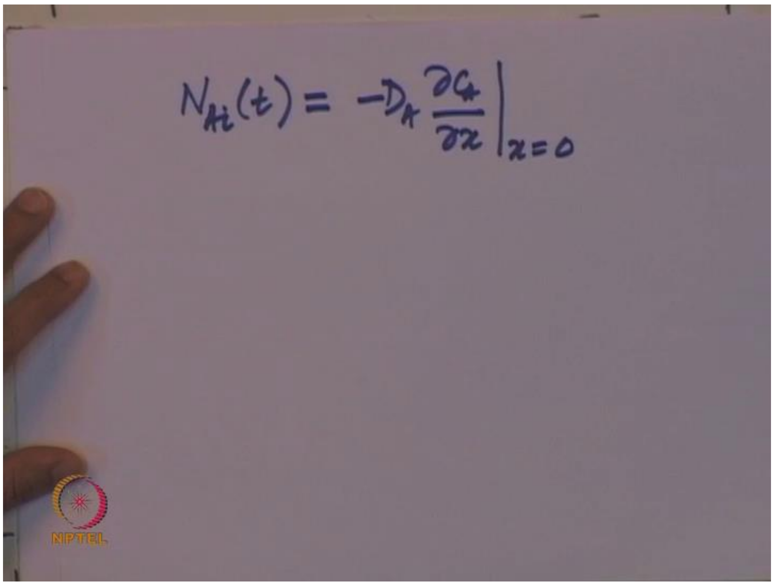

$$N_{At}(t) = -D_A \frac{\partial C_A}{\partial x}\bigg|_{x=0}$$

Let us say t second at the interface, we do this by applying fixed law as usual except that in this case because, we are dealing with a concentration profile that is the function of x as well as t, we have to use the partial derivative of concentration with respect to x evaluate DA t x equal to 0. So, we do this as follows.

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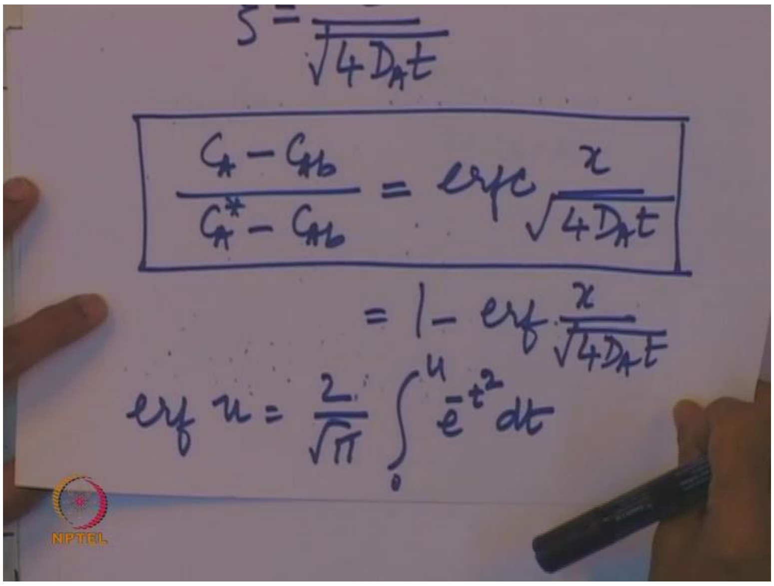

$$\xi = \frac{\quad}{\sqrt{4D_A t}}$$

$$\boxed{\frac{C_A - C_{Ab}}{C_A^* - C_{Ab}} = \operatorname{erfc} \frac{x}{\sqrt{4D_A t}}}$$

$$= 1 - \operatorname{erf} \frac{x}{\sqrt{4D_A t}}$$

$$\operatorname{erf} u = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} dt$$

We have the concentration profile as given by this expression here, if we differentiate this.

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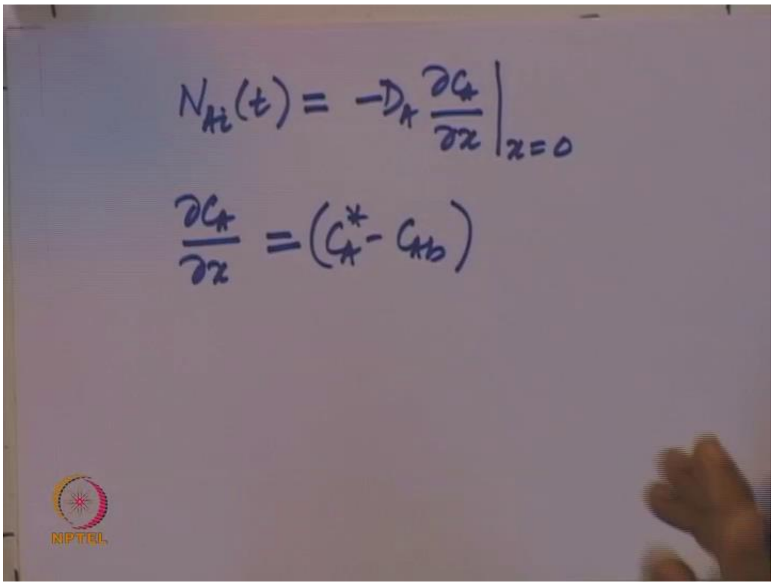

$$N_{Ai}(t) = -D_A \frac{\partial C_A}{\partial x}\bigg|_{x=0}$$

$$\frac{\partial C_A}{\partial x} = (C_A^* - C_{Ab})$$

We get D c a upon dx, we have to differentiate the error function here. So, we get first of all CA star minus CAB. And As usual we apply the chain rule of differentiation; differentiate the error function with respect to the argument and then differentiate the argument with respect to x.

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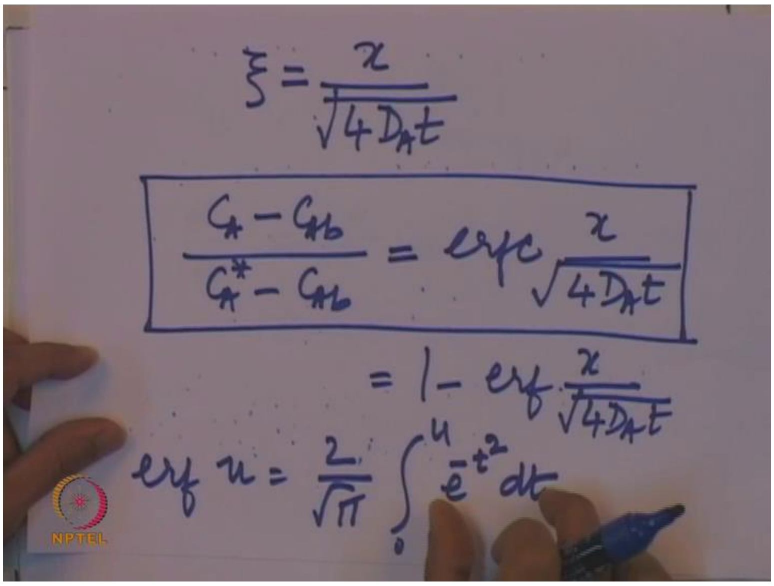

$$\xi = \frac{x}{\sqrt{4D_A t}}$$

$$\boxed{\frac{C_A - C_{Ab}}{C_A^* - C_{Ab}} = \operatorname{erfc} \frac{x}{\sqrt{4D_A t}}}$$

$$= 1 - \operatorname{erf} \frac{x}{\sqrt{4D_A t}}$$

$$\operatorname{erf} u = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} dt$$

So, when we do that the first. Differentiation of the error function with respect to the argument is simply the integrant itself evaluate DA t the upper limit.

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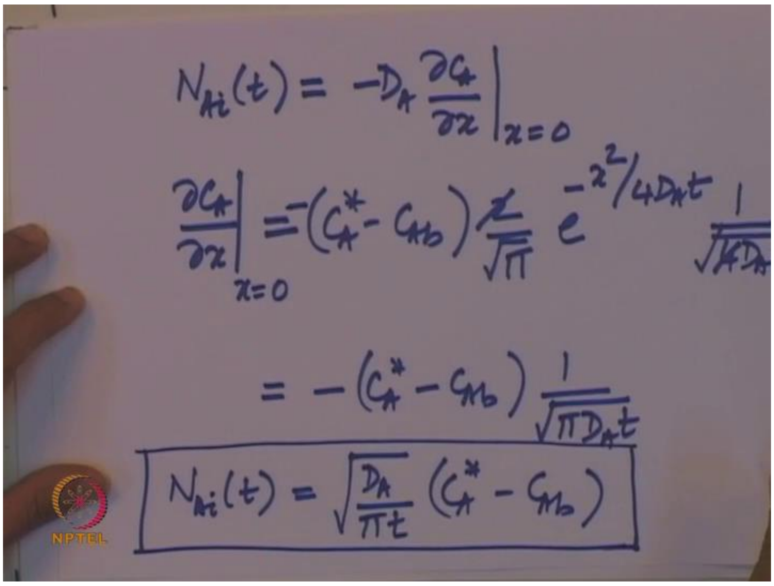

$$N_{Ai}(t) = -D_A \frac{\partial C_A}{\partial x}\bigg|_{x=0}$$

$$\frac{\partial C_A}{\partial x}\bigg|_{x=0} = -(C_A^* - C_{Ab}) \frac{2}{\sqrt{\pi}} e^{-x^2/4D_A t} \frac{1}{\sqrt{4D_A}}$$

$$= -(C_A^* - C_{Ab}) \frac{1}{\sqrt{\pi D_A t}}$$

$$\boxed{N_{Ai}(t) = \sqrt{\frac{D_A}{\pi t}} (C_A^* - C_{Ab})}$$

So, we get that as 2 by root pi e to the power minus x squared divided by 4 DAt. And differentiating the argument with respect to x we get 1 by square root of 4 DAt. So, the 2 will cancel with the square root of the 4 here and this whole thing has to be evaluate DA t x equal to 0; which means that we get there is a negative sign as well coming from the fact that we have the error function complement. And. So, we get minus CA star minus CAB 1 over root pi DAt. And substituting this in that expression over here we will get NA i of t as square root of DA upon pi t CA star minus CAB. So, this is the rate of absorption in an element, which has spent let us say t seconds at the interface. So, now, let us step back a moment and take stock at what we are trying to do.

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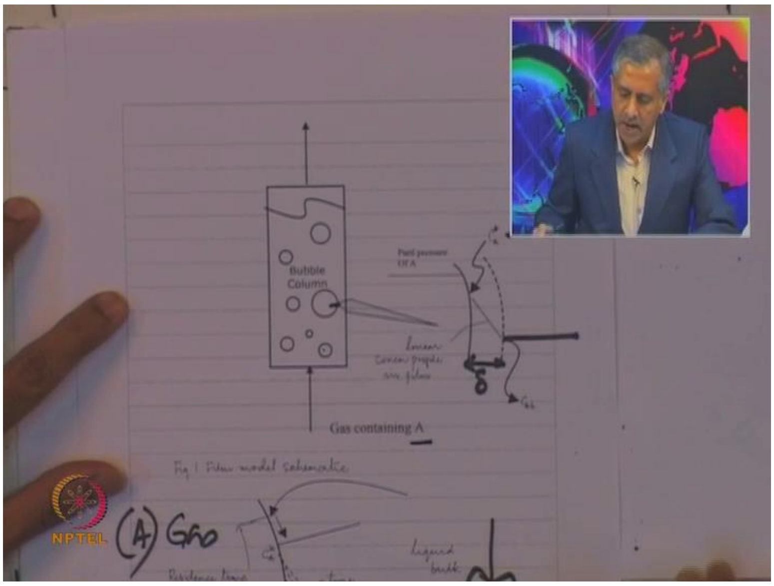

So, we start at with an operating piece of equipment such as the bubble column and then we said that we want to understand the local phenomena which are taking place at any location in this bubble column. Let us say, at a particular point on the surface of a typical bubble. Now, we are saying that even that particular point on the surface of a typical bubble is itself composed of several thousands of these what we have called surface elements and each of these elements has spent a different length of time absorbing at the interface.

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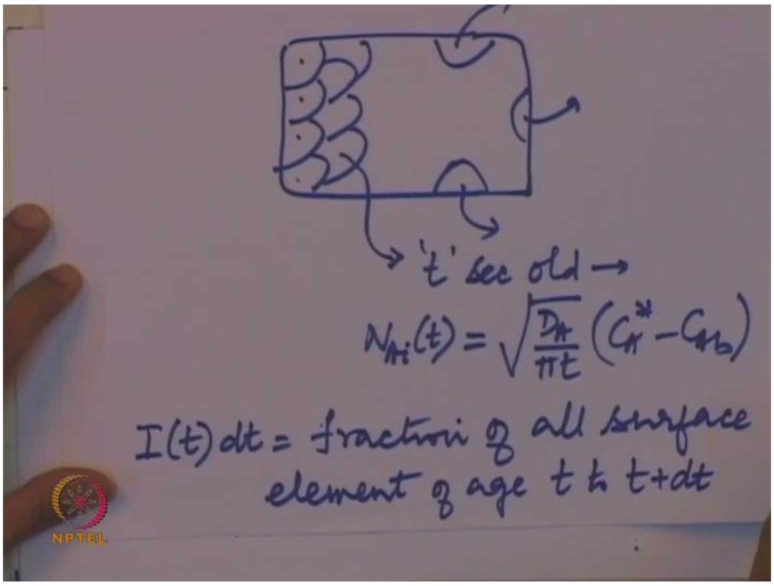

't' sec old →

$$N_{Ai}(t) = \sqrt{\frac{D_A}{\pi t}}\left(C_A^* - C_{Ab}\right)$$

I(t) dt = fraction of all surface element of age t to t+dt

In other words the interface itself, can be pictured you know this particular location on the surface of a bubble that, we are talking about if I want to spread that out in this manner then it is nothing but a Mosaique of surface elements which I can picture like this some of these surface elements might have just arrived some of these might have arrived a little earlier and so on. And there are those elements which are about to leave right.

So, there are short leaved elements there are I mean; there are elements which are just arrived that are elements, which have been absorbing for some time and there are elements which have been there a long time. So, what we have calculated on the previous slide is the absorption rate in a typical element of this kind which is if edge t. So, this absorbs we said at this rate. Now, if you want to calculate the rate at which the entire surface is absorbing then we need to know what part of the surface is how old.

In other words what fraction of the surface elements that makes up this unit interface, as spend what length of time at the interface. So, in order to do this, we define the age distribution function I of t d t which is the fraction of all surface elements of age t to t plus d t.

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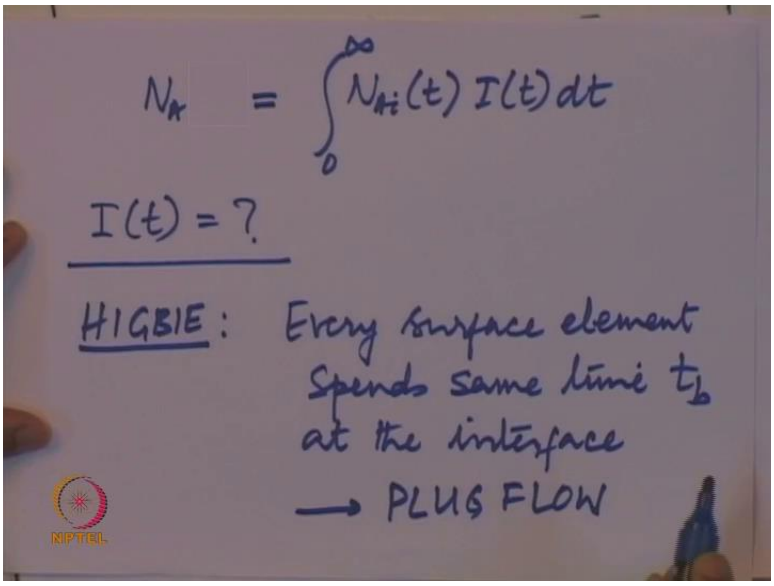

$$N_A = \int_0^\infty N_{Ai}(t)\, I(t)\, dt$$

$I(t) = ?$

HIGBIE: Every surface element Spends same time t_b at the interface

→ PLUG FLOW

If we define this internal age distribution as it is called then the average rate of absorption by the entire surface or average flux of absorption is given by. Integrating the instantaneous rate of absorption with respect to time waited with the internal age distribution function. So, what we are saying here is that this is the rate at, which an element of age t is absorbing. And this is the fraction of the surface which is of age t and therefore, the average rate of absorption of the entire surface is given by this expression.

Now, what do we use for this function i of t. So, this is where the difference between Higbie theory and Danckwerts theory plays out. So, we will consider these 2 concepts 1 by 1. So, if we consider, the Higbie version of the surface of the renewal theory what he said was that every element of every surface element every surface element spends exactly the same length of time at the interface spends the same time. And let us call that as t b at the interface this is the central assumption.

So, if you look at this assumption this is what happens in the plug flow an element enters into a plug flow environment spends exactly preorder amount of time which is decided by the volume of the plug flow environment divided by the volumetric flow rate. And there it leaves. So, since every liquid element is spending, the same length of time at the interface. So, as we have said this is similar to plug flow we can use the internal age distribution of a plug flow environment for i of t d t in order to calculate the average flux.

Now, if you go back to the residence time distribution theory then you will recall that for a plug vessel.

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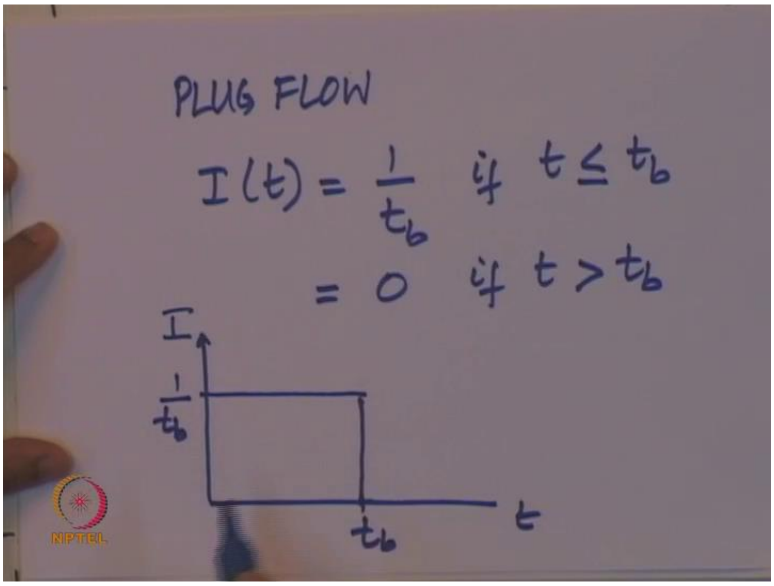

PLUG FLOW

$$I(t) = \frac{1}{t_b} \quad \text{if } t \le t_b$$

$$= 0 \quad \text{if } t > t_b$$

Plug flow environment the i of t function as this form, it is 1 over t b for t is less than or equal to t b and it is equal to 0 if t is greater than t b graphically this looks something like this. If you are plotting i as a function of time there is a time t b and this is the kind of distribution that we are talking about, there is nothing of age greater than t b and less than t b for every age there is an equal fraction. So, this is what is the inter aged distribution for a plug flow vessel and using this we can calculate NA.

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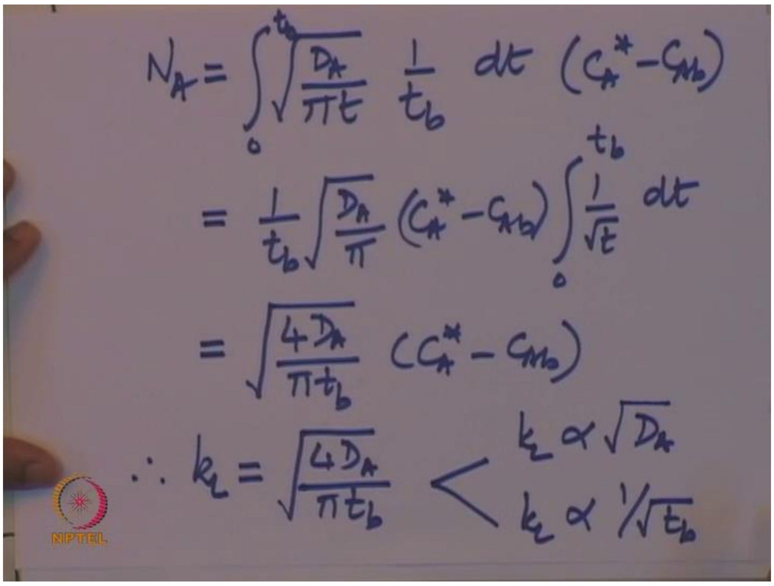

$$N_A = \int_0^{t_b} \sqrt{\frac{D_A}{\pi t}}\,\frac{1}{t_b}\,dt\,(C_A^* - C_{Ab})$$

$$= \frac{1}{t_b}\sqrt{\frac{D_A}{\pi}}\,(C_A^* - C_{Ab}) \int_0^{t_b} \frac{1}{\sqrt{t}}\,dt$$

$$= \sqrt{\frac{4D_A}{\pi t_b}}\,(C_A^* - C_{Ab})$$

$$\therefore k_L = \sqrt{\frac{4D_A}{\pi t_b}} < \begin{matrix} k_L \propto \sqrt{D_A} \\ k_L \propto 1/\sqrt{t_b} \end{matrix}$$

As NA i, which is square root of DA by pi t multiplied by the inter aged distribution and integrated from 0 to t b because, outside of t b for all time is greater than t b this function is 0. So, this is quite easy to evaluate, I have forgotten the CA star minus CAB which is of course, there. So, what we get is 1 over t b square root of DA by pi CA star minus CAB integral of 1 over root t d t 0 to t b. So, if you perform this integration the result is square root of 4 DA by pi t b into CA star minus CAB comparing this with the usual mass transfer rate expression, we find that the mass transfer coefficient in this theory interpreted as 4 DA by pi t b.

So, this has 2 things to say that k l is proportional to square root of DA number 1 and k l is inversely proportional to 1 over square root of the mean residence time at the interface. Now, Higbie was led to this model by consideration of a single bubble that lies through a quiescent column of liquid.

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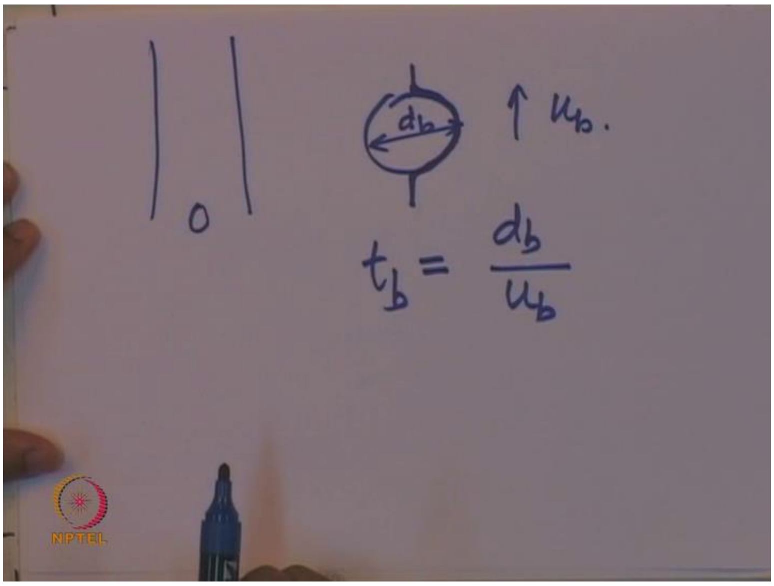

So, if we have a quiescent column of a liquid and let a single bubble arise, in such a column then it is easy to imagine that for every bubble leave liquid meets the bubble at the North Pole slights down the surface of the bubble and disingenuous from the bubble at the South Pole. So, if this is the kind of manner of contacting between gas and liquid then you can calculate that the time for which the gas is in contact with any element of liquid is nothing but the diameter of the bubble divided by the raised velocity of the bubble.

So, for these situations you can actually calculate t b from these kinds of considerations and plug it into this expression here. And therefore, you can actually do a prediction of k l. So, if you do that it turns out that the results are quite in a quad with experimental data and this equation bares itself out the quite credibly, but you can do this kind of a calculation t b only for very simple situation such as this. And the actual situation is then operating phase piece of process equipment is for more complexes.

The bubbles are do not raise in a single straight line they are moving in zig zag ways all over the place the liquid is not quiescent the liquid is itself turbulent motion. And in addition there are covalence and radiation process to which the bubbles are subject. So, in this kind of complex situation, it is not possible to calculate the value of t b from first principles.

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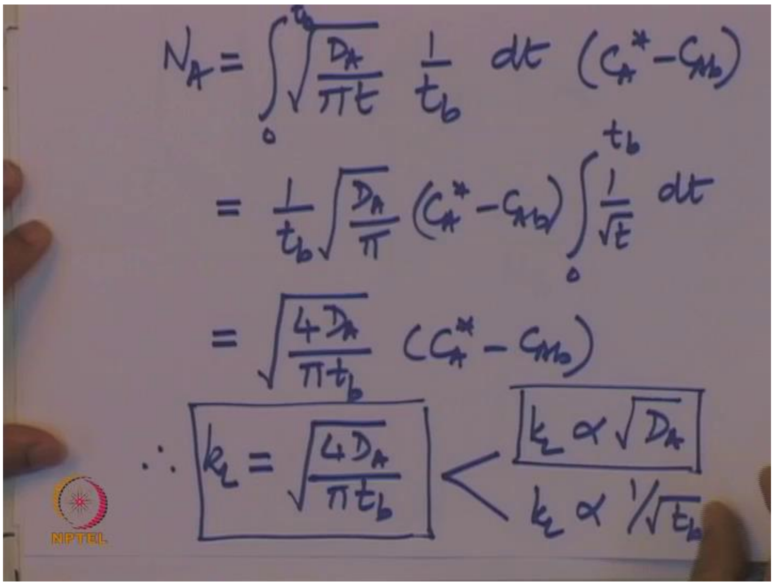

$$N_A = \int_0^{t_b} \sqrt{\frac{D_A}{\pi t}}\, \frac{1}{t_b}\, dt\, (C_A^* - C_{Ab})$$

$$= \frac{1}{t_b}\sqrt{\frac{D_A}{\pi}}\,(C_A^* - C_{Ab})\int_0^{t_b} \frac{1}{\sqrt{t}}\, dt$$

$$= \sqrt{\frac{4D_A}{\pi t_b}}\,(C_A^* - C_{Ab})$$

$$\therefore \boxed{k_L = \sqrt{\frac{4D_A}{\pi t_b}}} < \begin{array}{l} \boxed{k_L \propto \sqrt{D_A}} \\ k_L \propto 1/\sqrt{t_b} \end{array}$$

So, we should regard in those kinds of situations the equation as providing a definition for t b as much as the equation provides a definition for k l in other words what I am saying is t b is to be regarded as a fitting parameter to be calculated from experimental measured values of k l. So, if that is the case then this equation leaves just 1 testable prediction that is k l is proportional square root of diffusivity and we have already remarked at the beginning of while dealing with film theory this is quite in accordance with experimental date.

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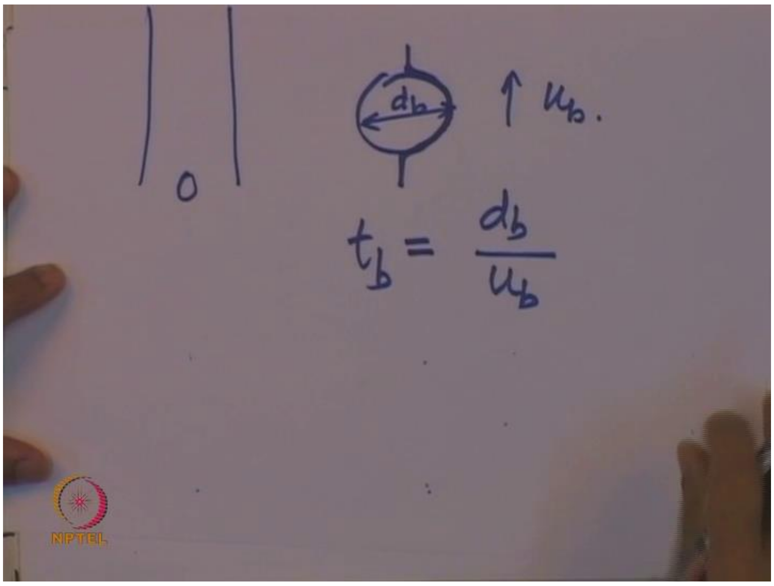

$$t_b = \frac{d_b}{u_b}$$

So, experimental date do bare out that the mass transfer coefficients are proportional to something like this square root of diffusivity. Now, let us look at what Danckwerts have to say about the surface age distribution and how the predictions of that theory are different from the Higbie theory.

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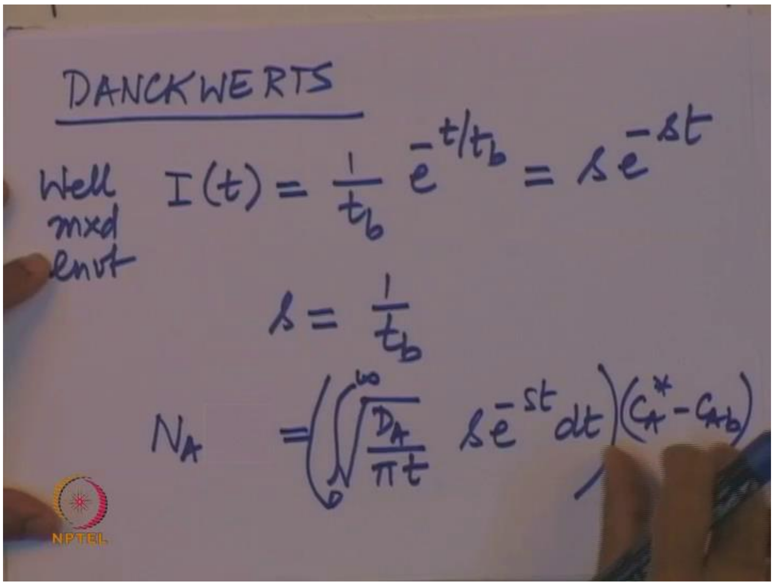

DANCKWERTS

Well mxd envt

$$I(t) = \frac{1}{t_b} e^{-t/t_b} = s e^{-st}$$

$$s = \frac{1}{t_b}$$

$$N_A = \left(\int_0^\infty \sqrt{\frac{D_A}{\pi t}} \, s e^{-st} \, dt \right) (C_A^* - C_{Ab})$$

So, Danckwerts surface renewal theory. So, what Danckwerts said was the Higbie is concept of plug flow of surface elements and every elements spending an exactly equal length of time at the interface is all right for very simple situations as single bubbles rising through the a quiescent column of liquid, but in actual operating pieces of equipment the situation is being for more complex elements of liquid are landing randomly at the interface. And they are randomly being taken away from interface.

So, the situation here is for more like in a well mixed vessel and very different from what it is plug flow vessel. So, he said why do not we look at the gas liquid interface as though it was well mixed environment. If that is the case we turn back to the residence time distribution theory and see what it has to say about the distribution of inter ages for well mixed environments. And there we come up on this kinds of an expression i of t for a well mixed environment i of t is given by 1 over t b e to the power minus t upon t b.

Or this is written in the language of Danckwerts theory in that manner, where s what Danckwerts called as a surface renewal rate is nothing but the reciprocal of the mean residence time. So, that is the internal age distribution that we have to use in consumption with instantaneous rate of absorption in order to predict the average rate of absorption which therefore, for this theory takes on this form DA divided by pi t that is the instantaneous rate of absorption multiplied by s into e to the power minus s t d t.

The whole thing integrated from 0 to infinity and we have to add the driving force term which is the part of the NA t DA by pi t under the square root multiplied by CA star minus CAB. So, when we do this.

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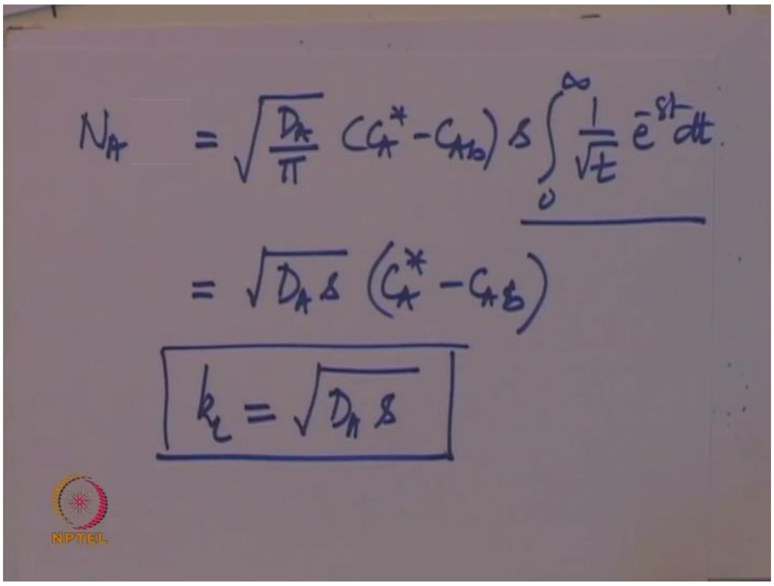

$$N_A = \sqrt{\frac{D_A}{\pi}}\,(C_A^* - C_{Ab})\, s \underline{\int_0^\infty \frac{1}{\sqrt{t}}\, e^{-st}\, dt}$$

$$= \sqrt{D_A s}\,(C_A^* - C_{Ab})$$

$$\boxed{k_L = \sqrt{D_A s}}$$

So, this you know if we take the constant elements out then we see that it is nothing but square root of DA upon pi CA star minus CAB into s integral 0 to infinity 1 over root t e to the power minus s t d t. Now, the simplest way to evaluate this integral is to recognize that this is nothing but the Laplace transform 1 over square root of t. So, if you look up the Laplace transform of 1 over square root t from a table of Laplace transforms. And substitute we will find that this amounts to root of DA s multiplied by CA star minus CAB.

Comparing this with the mass transfer rate expression, we find that the Danckwerts theory predicts k l as being able being equal to square root of DA s. So, we have this and we have the earlier expression due to Higbie and if we compare this and this 2 things are obvious 1 is the square root of DA dependence is there in both of them.

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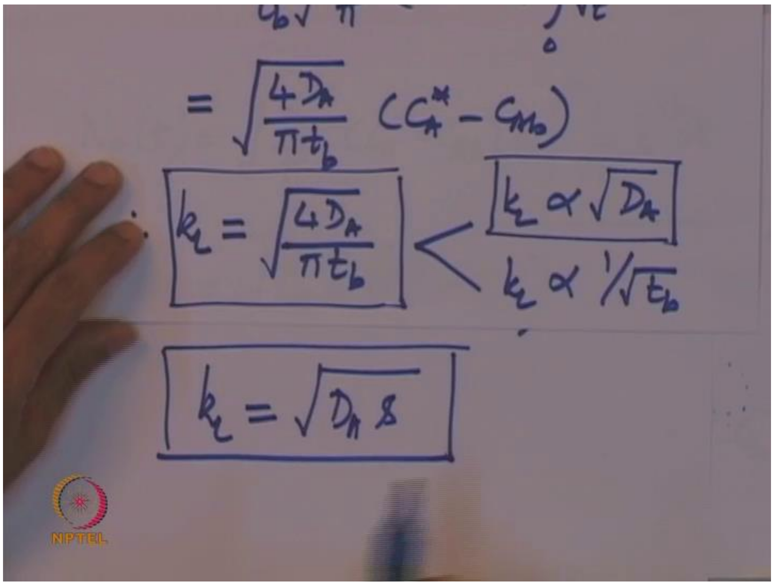

$$= \sqrt{\frac{4D_A}{\pi t_b}}\,(C_A^* - C_{Ab})$$

$$\therefore \boxed{k_L = \sqrt{\frac{4D_A}{\pi t_b}}} < \boxed{k_L \propto \sqrt{D_A}}$$

$$k_L \propto 1/\sqrt{t_b}$$

$$\boxed{k_L = \sqrt{D_A s}}$$

And. In fact, if you look at the way in which we are doing these integrations it does not matter.

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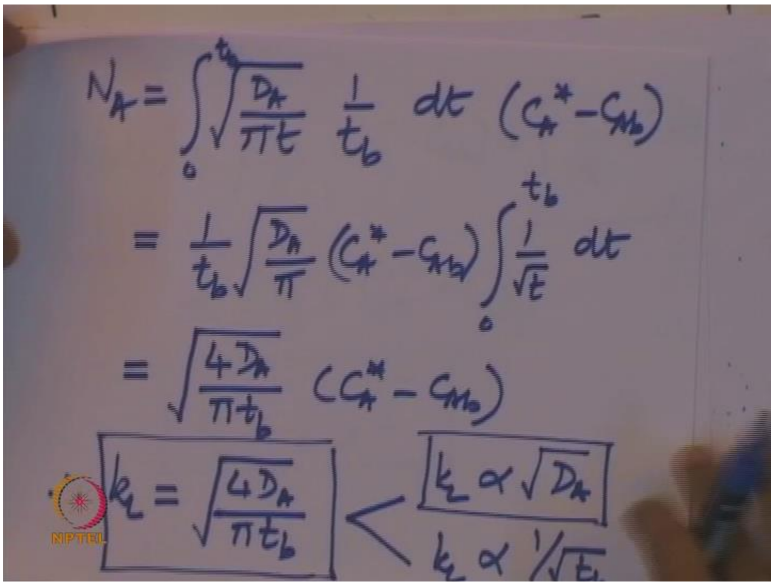

$$N_A = \int_0^{t_b} \sqrt{\frac{D_A}{\pi t}}\,\frac{1}{t_b}\,dt\,(C_A^* - C_{Ab})$$

$$= \frac{1}{t_b}\sqrt{\frac{D_A}{\pi}}\,(C_A^* - C_{Ab})\int_0^{t_b} \frac{1}{\sqrt{t}}\,dt$$

$$= \sqrt{\frac{4D_A}{\pi t_b}}\,(C_A^* - C_{Ab})$$

$$\boxed{k_L = \sqrt{\frac{4D_A}{\pi t_b}}} < \boxed{k_L \propto \sqrt{D_A}}$$

$$k_L \propto 1/\sqrt{t_b}$$

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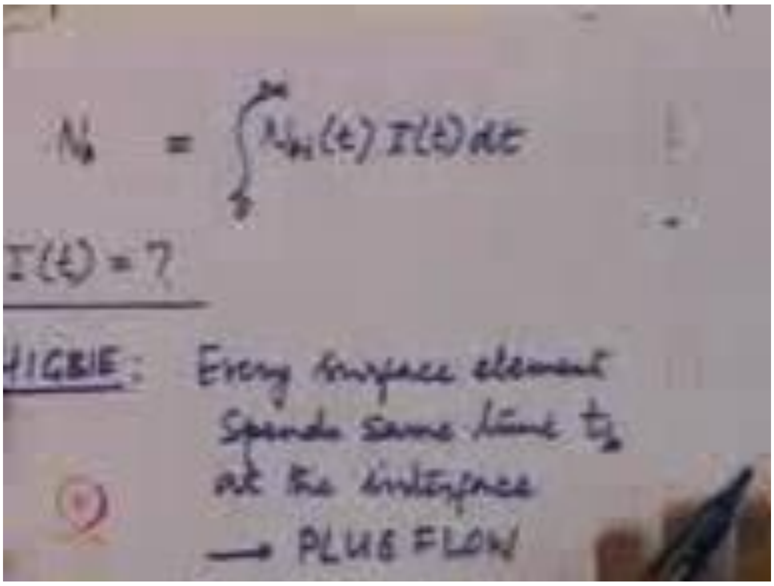

$$N_A = \int_0^\infty N_{Ai}(t)\, I(t)\, dt$$

$I(t) = ?$

HIGBIE: Every surface element spends same time t_b at the interface

→ PLUG FLOW

It does matter as to what you assume for this function i of t d t the square root of DA dependence comes from within the expressions from NA i of t. And therefore, that is not going to change irrespective of what you substitute for i of t d t. So, it is not surprising that both Higbie and Danckwerts theory predict that k l is proportional square root of DA and in that respect therefore there is nothing to distinguish 1 one theory from the other.

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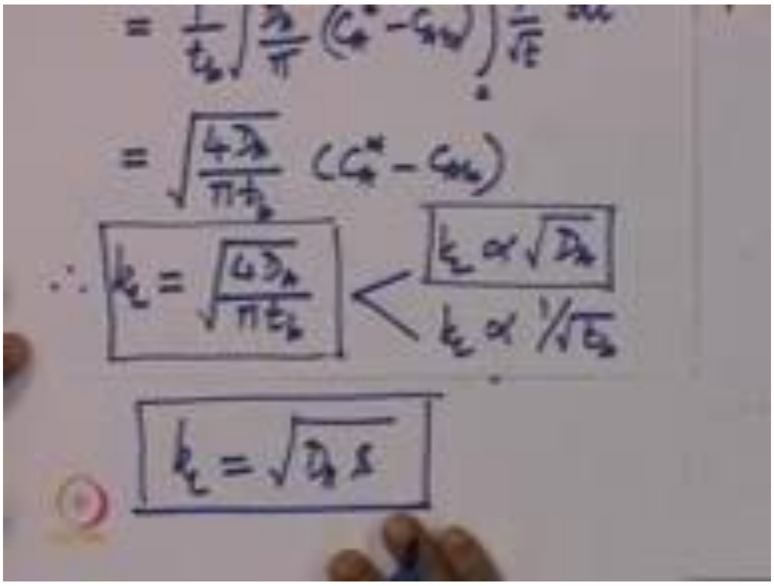

$$= \frac{1}{t_b}\sqrt{\frac{D_A}{\pi}}\,(C_A^* - C_{Ab}) \int \frac{1}{\sqrt{t}}\, dt$$

$$= \sqrt{\frac{4D_A}{\pi t_b}}\,(C_A^* - C_{Ab})$$

$$\therefore \boxed{k_L = \sqrt{\frac{4D_A}{\pi t_b}}} < \begin{array}{l} \boxed{k_L \propto \sqrt{D_A}} \\ k_L \propto 1/\sqrt{t_b} \end{array}$$

$$\boxed{k_L = \sqrt{D_A s}}$$

As to the other prediction of whether k l is universally proportional to square root of t b both of these do predict an universe proportionality between square root t b there is a constant here that is not very different from 1 which is the only difference between the Higbie theory and Danckwerts theory. So, all in all there does not seems to be very much that distinguishes the Danckwerts theory from the Higbie theory especially, when you consider that this t b something that cannot be measured from first principles and therefore, the only way you can fix t b is to actually go back to a measured value of the mass transfer coefficient.

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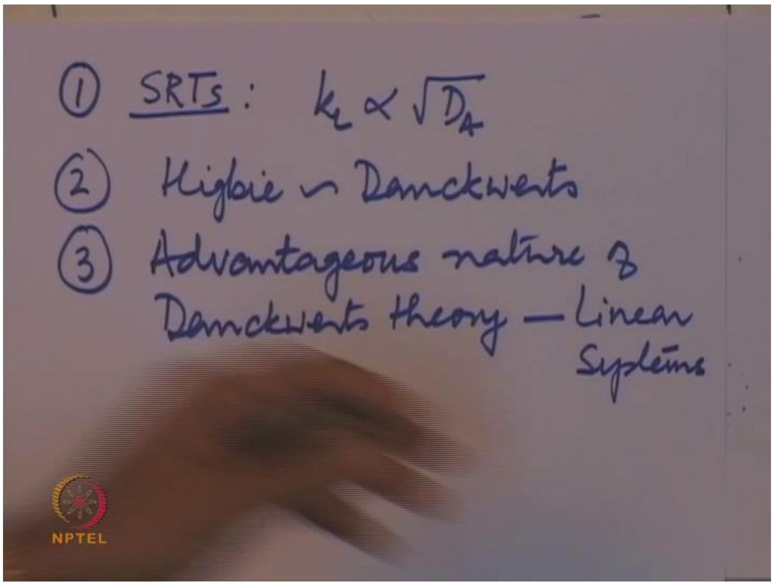

① SRTs : $k_L \propto \sqrt{D_A}$

② Higbie ~ Danckwerts

③ Advantageous nature of Danckwerts theory — Linear Systems

So, we will conclude this section by making some concluding remarks on the 2 theories that we have seen, under the surface renewal category the first remark we make is that in the surface renewal theories. It is a given that k l is proportional to square root of DA. And in that respect these theories are better than the film theory, which predicts that k l is proportional to DA to the power 1 linearly to proportional to DA. And the second thing is that the Higbie theory and the Danckwerts theory are somewhat similar in terms of their quantitative predictions of the mass transfer coefficient.

There being a difference of about 10 percent, if the value of t b is exactly known given that the value of a t b is not known and it can only be obtained from experiments, there is you can say that the Higbie theory and Danckwerts theory are virtually saying the same thing the third point is if that is the case and the Danckwerts theories seems to be more complicated in terms of the internal like distribution function its uses why worry about the Danckwerts theory at all.

The real advantageous of the Danckwerts theory is mathematical advantageous nature of Danckwerts theory surfaces, when you have got linear systems to consider such as the simple mass transfer problem that we have considered so far.

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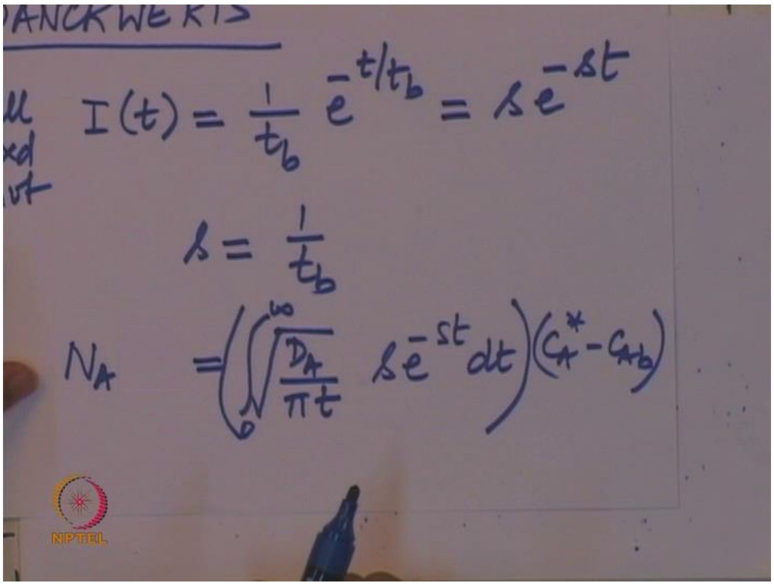

ANCKWERTS

$$I(t) = \frac{1}{t_b} e^{-t/t_b} = s e^{-st}$$

$$s = \frac{1}{t_b}$$

$$N_A = \left(\int_0^\infty \sqrt{\frac{D_A}{\pi t}}\, s e^{-st}\, dt\right)\left(C_A^* - C_{Ab}\right)$$

That arises, when you look at this integral here and we made the point that the way to evaluate this. Integral is to recognize the parallel between the averaging process that is going on here and Laplace transformation. So, what that this suggest is that if you have a situation in which the governing equations can be solved by Laplace transforming the equation remember that the governing equation in the surface renewal theories is always going to be a partial differential equation. And 1 of the techniques of solving partial differential equations which are linear is to Laplace transform the equations with respect to time and eliminate time and converts this to an ordinary differential equations.

So, if you use that technique and get the equations in the Laplace domain as an ordinary differential equation and solve it then the required quantities, which are flux the concentration profile etcetera the average concentration profile etcetera can be obtained without actually inverting the transform to back to the time domain and you can work in the Laplace domain as itself and directly obtain the results. So, this gives you an advantage in terms of the mathematical aspects of solving the differential equations that arise. So, we will conclude by summarizing the important aspects of today’s lecture.

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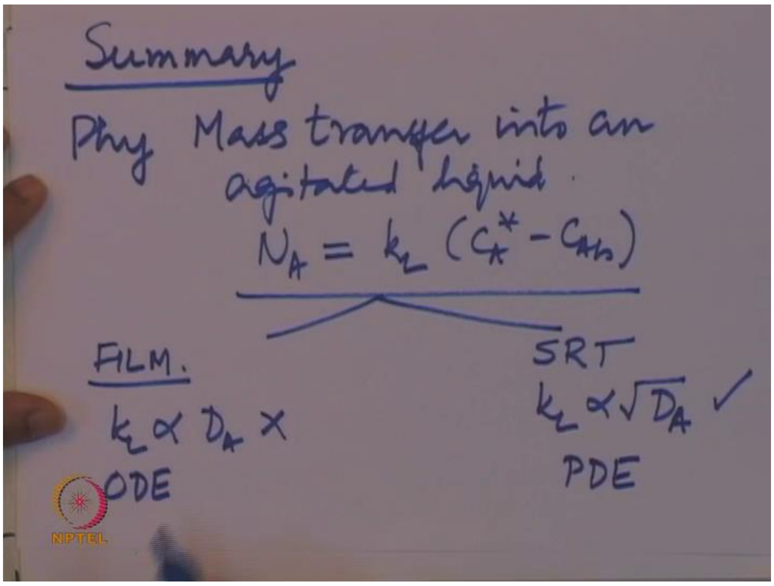

Summary

Phy Mass transfer into an agitated liquid.

$$N_A = k_L (C_A^* - C_{Ab})$$

FILM.

$k_L \propto D_A$ ×

ODE

SRT

$k_L \propto \sqrt{D_A}$ ✓

PDE

So, we considered the problem of mass transfer or what we may call as physical mass transfer because, there is no reaction here into an agitated liquid. Experimentally this situation is always explained using in mass transfer coefficient and usual way in which the absorption flux is written is to invoke a mass transfer coefficient And A driving force of this kind. So, this is how experimentally, we describe the physically mass transfer into an agitated liquid.

So, we considered 2 theories 1 is the film theory and the film theory said that the k l is proportional to diffusivity. We considered the surface renewal theories. And the surface renewal theory is said that k l is proportional to square root of diffusivity. Now, this is more correct when you look at the evidence that is available of the way in which mass transfer coefficient dependence on diffusivity and this is not, so correct; however, the advantage here is that there are ordinary differential equations to solve and here there are partially partial differential equations to solve.

Therefore, from the mathematical point of view, if we can use this theory based on some consideration it is going to be always easier to solve. So, we will keep that in mind and in the next lecture, when we take up the effect of chemical reaction on the mass transfer rate we will first do our deliberations in terms of the film theory. We will disregard from the movement that the film theory is less realistic as compared surface renewal theories.

We will assume that the film theory is a model that is acceptable in some sense and then we will look at the effect of chemical reaction on the physical mass transform.

We will go through the development and then we will see how the development will differ, if we were to use surface renewal theories. Then it will turn out that if all your interested in is in predicting the effect of mass transfer effect on effect on mass transform of the chemical reaction then 1 theory is nearly as good as another having said that there are some kinds of reactions for which the surface renewal variety of theories. We will give a better prediction as compare to the film theory.

So, we will come to those aspects as we go a long, but I have made these comments just to justify my use of the film theory in the initial sections of the consideration of chemical reaction and its effect on mass transform.