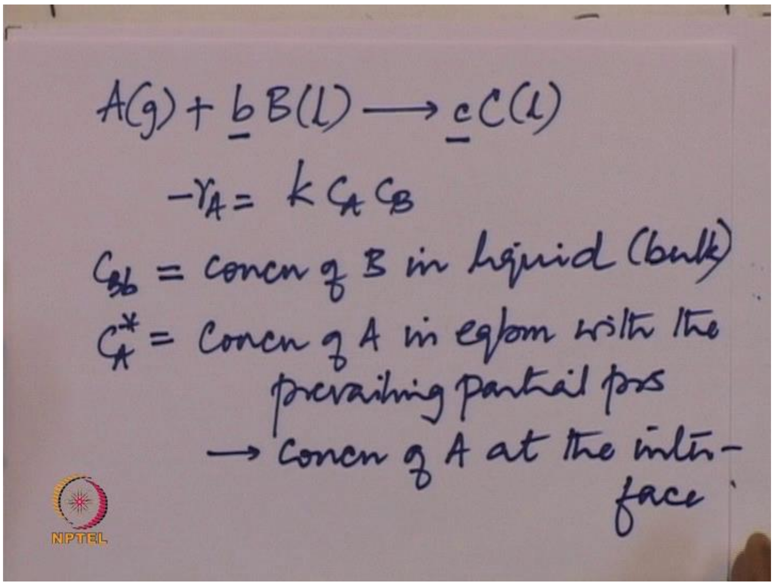
Chemical Reactions Engineering II
Prof. A. K .Suresh
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 21
GLR-2: Effect of chemical reaction on mass transfer: the slow reaction regime

Welcome back, in the last lecture we looked at the mechanism of mass transfer from a gas 2 energy catalytic liquid and we considered 2 theories which seek to explain this phenomenon, the 2 theories the first of which was the film theory and the second the surface renewal theories. These 2 theories start from very different stand points and the mechanisms that are postulated for the mass transfer process or also quite different and not surprisingly, the mathematics also works out quite differently.

And we end of with 2 different expressions for the mass transfer coefficient from a gas to a liquid. Now in the ultimate analysis, neither of these theories able to predict the mass transfer coefficient from first principles, but as we shall see, the main utility of theories is in their ability to predict the effect of mass transfer, a effect of chemical reaction on mass transfer. So, this is what we are going to concentrate on in the present lecture as well as in some other lectures to follow. So, the situation is something like this there is a gaseous solute a which is getting absorbed into a liquid be liquid solution and liquid contains a component b with which a can react.

(Refer Slide Time: 01:48)



$A(g) + \underline{b}B(l) \longrightarrow \underline{c}C(l)$

$-r_A = k C_A C_B$

C_{Bb} = concn of B in liquid (bulk)

C_A^* = Concn of A in eqbm with the prevailing partial press

$\longrightarrow$ Concn of A at the inter-face

So, we write the stoichiometry of reaction as A from the gas phase reacting with B from the liquid phase giving raise to C and all though it does not really matter all that much. We will assume that the C remains dissolved in the liquid phase and B and C are stoichiometric coefficients. And we shall assume that this reaction has intrinsic rate which is first order in A and first order in B. As usual as did in the case of the physical mass transfer we will assume that there is no gas phase resistance entire resistance to the mass transfer is concentrated on the liquid side.

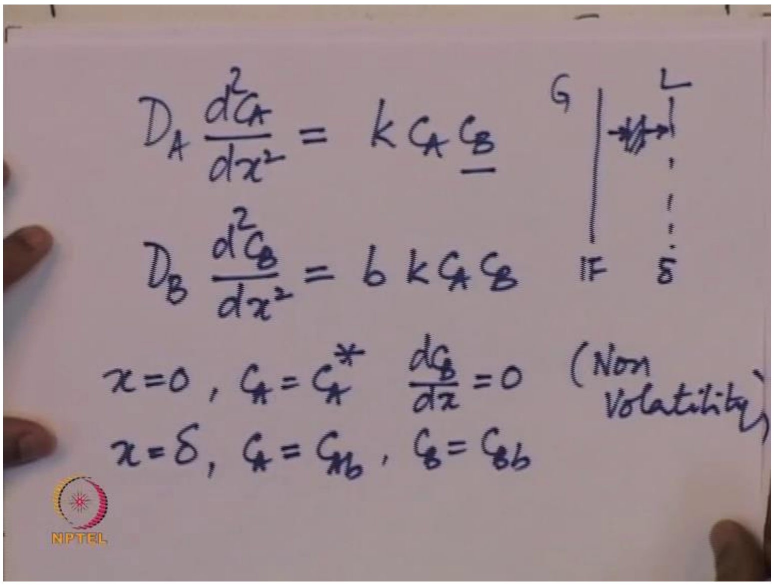
So, we shall loosen these assumptions towards the later stages of this topic, both the assumption with respect to the orders of the reaction as well as with respect to the nonexistence of gas phase resistance. And we will see the consequences of those at that point, but at this point I will make this make these assumptions in order to keep the a focus on the essential aspects and a keep the other details simple. We will further assume a that, the film theory is good enough to explain this process of mass transfer with chemical reaction.

So, why will have outside earlier, that in view of the available evidence the surface renewal theories are to be trusted more than the film theory; in view of the simplicity of the film theory, we will do the development first in the framework of the film theory. And later on we will see what differences come of out, if it is the surface renewal theory is that we invoke and we shall also a give a justification for why film theory still useful inspect of the fact that the prediction it makes about, the way the mass transfer coefficient depends on diffusivity is not borne out by the available experimental data.

So, we shall proceed with the analysis of this process, so A is getting transferred from the gas phase to the liquid and on the liquid site: where it diffuses into the liquid site it reacts, with 1 of the components of the liquid phase which we have called as B. The concentration of this B in the bulk liquid we take it as C Bb and C Bb is the concentration of b in liquid bulk that is to say outside the film.

And CA star is the concentration of A in equilibrium with the prevailing partial pressure and within the film theory partial therefore, this is also the concentration of A at the interface.

(Refer Slide Time: 05:30)



$$D_A \frac{d^2 C_A}{dx^2} = k C_A \underline{C_B}$$

$$D_B \frac{d^2 C_B}{dx^2} = b k C_A C_B$$

$x = 0$, $C_A = C_A^*$ $\frac{dC_B}{dx} = 0$ (Non Volatility)

$x = \delta$, $C_A = C_{Ab}$, $C_B = C_{Bb}$

So, with those notations having been agreed upon a we can write the diffusion reaction equations that govern the diffusion of A into B a; a into the liquid rather in the following manner DA d square CA by dx squared equals k CA CB, which is the same equation has we had worked with before except for the presence of this reaction rate. So, what this is saying is that, if you look at the film which this is the gas liquid interface, that is the gas site and this is the liquid site and that is a film.

So, in any differential slice of the film there is rate at which the solute is a entering by diffusion, there is rate at which is the solution is leading by diffusion. The difference between these 2 rates is consume by chemical reaction within this slice.

So, we had a 0 here when there was no reaction. So, whatever was entering was equal to the rate at which it was leaving, but now there is there is rate at which the material enters at x and there is a lower rate at which materials leaves at x plus delta x and this difference is consume by reaction. That is all that is happening, because this is the study state theory and there is no accumulation.

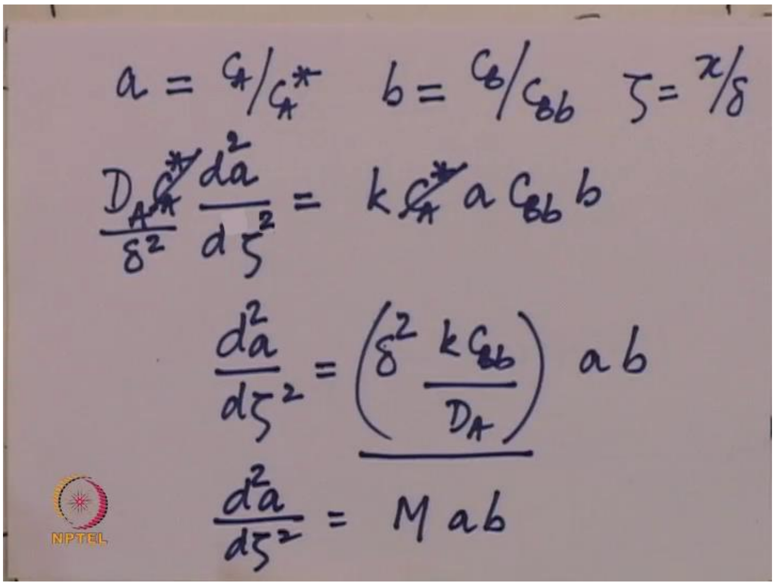
So, input minus output equals consumption. So, that is what this reaction is this, this equation is saying. Now, this equation a cannot be solved by itself, because it contains the concentration of B and it is possible that the concentration of B also has a profile within the film. In order to describe that profile, we have to write a very similar equation for B it is almost identical except for the fact that we use the diffusivity of B instead of the diffusivity of A in this equation.

So, this is input minus output of B into the a differential slice. And the reaction rate term contains the stoichiometric factor is addition to the rate term that was present in the equation for A. That is, because rate at rate of consumption of B is lower case b times the rate of consumption of A. Consistent with the postulates of the film theory, the boundary conditions can be written in the following manner at x is equal to 0 we have CA be given by CA star.

And at x is equal to delta; this is delta CA is given by CA bulk. And when it comes to the boundary conditions for B at x is equal to delta the concentration of B is C Bb as we have already assumed at x is equal to 0 we make the assumption of non-volatility. That is to say, we assume that B has no tendency to pass over on to the gas site by a vaporization. And what this means is that, the flux of B at the gas liquid interface is 0 and if you invoke fix law for flux what this means is that, we have saying d CB by dx is equal to 0, because it is product of this with the diffusivity that determines the flux.

And since we are saying the flux is 0 this gradient must be 0 at the gas liquid interface. So, this is the formulation of the problem that is diffusion equation that governs the transport A, this is the diffusion equation that governs the transport of B and these are the relevant boundary conditions the with which these equations have to be solved. Now if you look at these equations, there are concentrations, there are distances, and these are in different units, and they have different magnitudes. Therefore, in order to analyze the effect of this chemical reaction on the mass transfer. And particularly, in order to understand the effect of chemical reaction as the chemical reaction rate is varied relative to the diffusion rate. It is far more useful to treat these equations in a dimension less form.

(Refer Slide Time: 10:08)



$$a = C_A/C_A^* \quad b = C_B/C_{Bb} \quad \zeta = x/\delta$$

$$\frac{D_A \cancel{C_A^*}}{\delta^2}\frac{d^2a}{d\zeta^2} = k\cancel{C_A^*}\, a\, C_{Bb}\, b$$

$$\frac{d^2a}{d\zeta^2} = \underline{\left(\delta^2 \frac{kC_{Bb}}{D_A}\right)}\, a\, b$$

$$\frac{d^2a}{d\zeta^2} = M\, a\, b$$

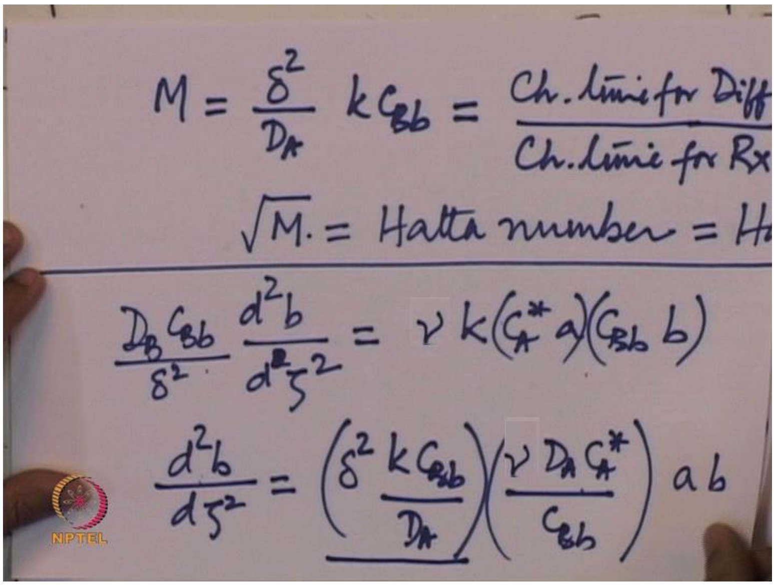
A let us do that, by defining the following non-dimension variables let us call lower case a as the non-dimensional concentration of a is obtained by dividing the concentration of A divided by the concentration of A at the interface. Similarly, is b is concentration of b divided by concentration of b in the bulk may be what we should do is in order to avoid confusion between this b and the stoichiometric factor b. We will consider the stoichiometric factor as new other words, we go back I can change this stoichiometric coefficient to new the Greek letter new.

So, that there is no confusion between the 2 sets of symbols that we have using. And we are left with the independent variable that is distance and we shall let zeta; the Greek letter zeta stand for non-dimensional distance which we obtained by dividing the x the value of x by the maximum value that x can take namely delta. So, what we see in this scheme of non dimensionalization is at each variable is being divided by the maximum value it can take.

And therefore, the non-dimensional variables will have a value between 0 and 1, so there all comparable. So, earlier in the dimensional form they need not have been comparable right now they are. And substituting these into the differential equations we can do the non dimensionalization as follows DA we have got d CA that is d a multiplied by CA star this is second derivative.

And we have got a second derivative of x which becomes delta squared times b squared a zeta equals k CA is CA star times a and CB is CB bulk times b. So, the CA star will get canceled and we can rearrange this equation to read as follows delta squared k C Bb divided by DA multiplied by a b. So, I shall call this group as M and write this equation as d squared a upon d zeta squared equals M ab.

(Refer Slide Time: 13:13)



$$M = \frac{\delta^2}{D_A} k C_{Bb} = \frac{\text{Ch. time for Diff}}{\text{Ch. time for Rx}}$$

$$\sqrt{M}. = \text{Hatta number} = H$$

$$\frac{D_B C_{Bb}}{\delta^2} \frac{d^2 b}{d\zeta^2} = \nu k (C_A^* a)(C_{Bb} b)$$

$$\frac{d^2 b}{d\zeta^2} = \underline{\left(\delta^2 \frac{k C_{Bb}}{D_A}\right)}\left(\frac{\nu D_A C_A^*}{C_{Bb}}\right) a b$$

So, what is the let us stop for a movement and consider the meaning of this dimensionalzed group that we have defined here M; which is delta squared divided by DA multiplied by k C Bb. And if you look at this k C Bb is a pseudo first order rate constant for the reaction. And the reciprocal of the first order rate constant has a significance of a characteristic time for reaction. That is the time that is required by the reaction to proceed to a significant extent.

So, 1 over k C Bb is the characteristic time for reaction and delta squared by DA is the characteristic time for diffuse. Because, delta squared is the square of the distance over which the diffusion is occurring and DA is diffusivity which has units. So, centimeter square per second or meter square per second and therefore, this is the characteristic time for diffusion. In other words, this parameter M compare the characteristic time for diffusion with the characteristic time for reaction or it is comparing the reaction rate with the diffusion rate.

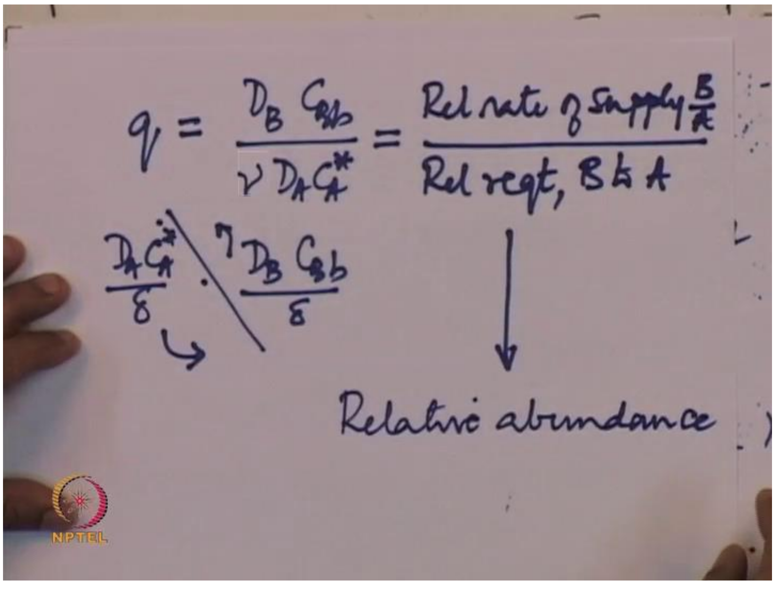
So, if M is large it means that, the characteristic time for diffusion is much larger than the characteristic time for reaction or reaction is much faster than diffusion. If M is small it means, the characteristic time of diffusion is much smaller than the characteristic time for reaction; which means, the diffusion is a much faster process than reaction. So, by varying M we can looking at reactions of varying grades relative to the rate of diffusion.

In the literature square root of M has come to the called as Hatta number and in some books you will see this being refer to as Ha and we shall use the nomenclature M because much of the literature continuous to use that kind of nomenclature. So, we have got the non-dimensional form of the diffusion equation for A in that manner.

We can do the same thing for diffusion equation for B and here we get d squared b divided by delta squared here and d squared to zeta d zeta squared equals mu K CA star a C Bb b all right. This is the concentration of A and this is concentration of B and that is the rate. So, in order to express this equation also in terms of this dimensional less number that we have defined, we will group these various quantities that we have obtained here in the following manner, multiplied by mu DA CA star divided by C Bb into a times b.

So, we say that in the equation for b this familiar quantity has made it appearance. There is in additional dimensional less group that has a arise, let us see what is the meaning of this additional group that has made its appearance now.

(Refer Slide Time: 17:16)



$$q = \frac{D_B C_{Bb}}{\nu D_A C_A^*} = \frac{\text{Rel rate of supply } \frac{B}{A}}{\text{Rel reqt, B to A}}$$

$$\frac{D_A C_A^*}{\delta} \; > \; \frac{D_B C_{Bb}}{\delta}$$

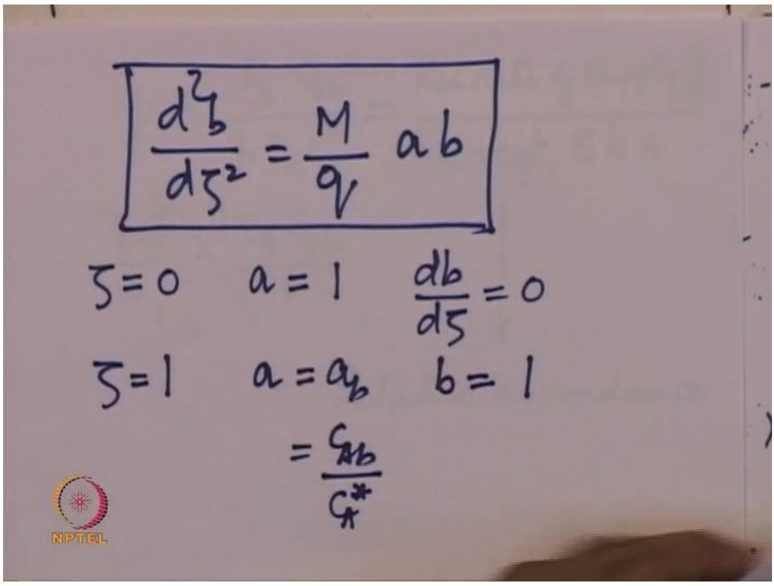
Relative abundance

.

So, let us call q as the reciprocal of that group. So, by q let us denote this quantity DB C Bb divided by mu DA CA star. So, what does this represent? DB C Bb divided by mu DA CA star is the relative rate of supply of b to the rate of supply of a. That is, because in on the maximum supply of A can be written in that manner which is nothing but the mass transfer coefficient of A multiplied by the maximum driving force that is possible. And the similarly, the maximum rate of supply of b would be DB C Bb divided by delta and.

So, it is the ratio of these quantities that going to the numerator and this coming to the denominator that is appearing here. That is being divided by the stoichiometric factor b, which is the number of moles of b that is require by the reaction per mole of a. So, we can regard this as the relative rate of supply B to A divided by relative requirement B to A. So, because of this definition we can associate the significance of relative abundance to the parameter q and we will continue to denote by this letter q.

(Refer Slide Time: 19:16)



$$\boxed{\frac{d^2 b}{d\zeta^2} = \frac{M}{q}\, a b}$$

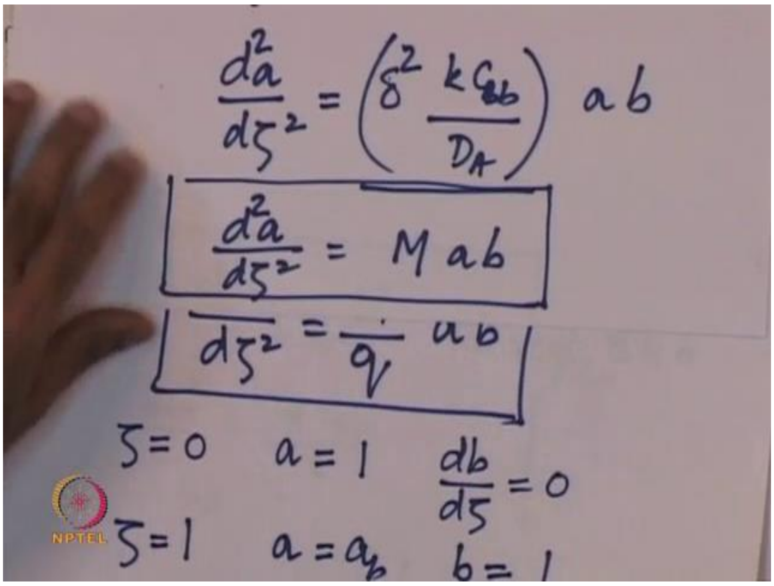
$\zeta = 0 \quad a = 1 \quad \frac{db}{d\zeta} = 0$

$\zeta = 1 \quad a = a_b \quad b = 1$

$= \frac{C_{Ab}}{C_A^*}$

So, with that definition we can now write the equation for b as d squared b upon d zeta squared equals M divided by q multiplied by a times b. So, we have the equation for a we have the equation for b it is a simple matter to write the non-dimensional boundary conditions x equal to zeta corresponds to x equal to 0 corresponds to zeta equal to 0. And at that point a equals 1 and the equation for b is db by d zeta equal to 0 and at zeta equal to 1; which is the end of the film a is ab which is nothing but the concentration of A in the bulk divided by the concentration at interface and the concentration of b in non-dimensional terms is 1.

(Refer Slide Time: 20:16)



$$\frac{d^2 a}{d\zeta^2} = \left(\delta^2 \frac{k C_{Bb}}{D_A}\right) a b$$

$$\boxed{\frac{d^2 a}{d\zeta^2} = M a b}$$

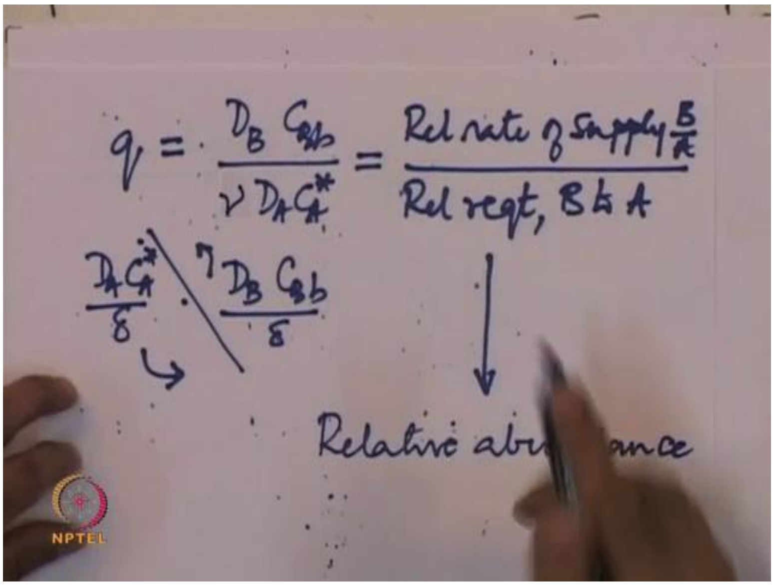
$$\boxed{\frac{\quad}{d\zeta^2} = \frac{\cdot}{q} a b}$$

$\zeta = 0$ $a = 1$ $\frac{db}{d\zeta} = 0$

$\zeta = 1$ $a = a_b$ $b = 1$

So, we have got the equation for a, we got the equation for b and we have the initial boundary conditions. And now we are ready to look at the implications of these equations on the rate of mass transfer. So, in order to understand the various things that can happen when reactions of various velocities take place in conjunction with mass transfer; instead of directly going ahead and solving these equations by Brute force method. Let us do some analysis and a see what happens.

(Refer Slide Time: 20:53)



$$q = \frac{D_B C_{Bb}}{\nu D_A C_A^*} = \frac{\text{Rel rate of supply } \frac{B}{A}}{\text{Rel reqt, B to A}}$$

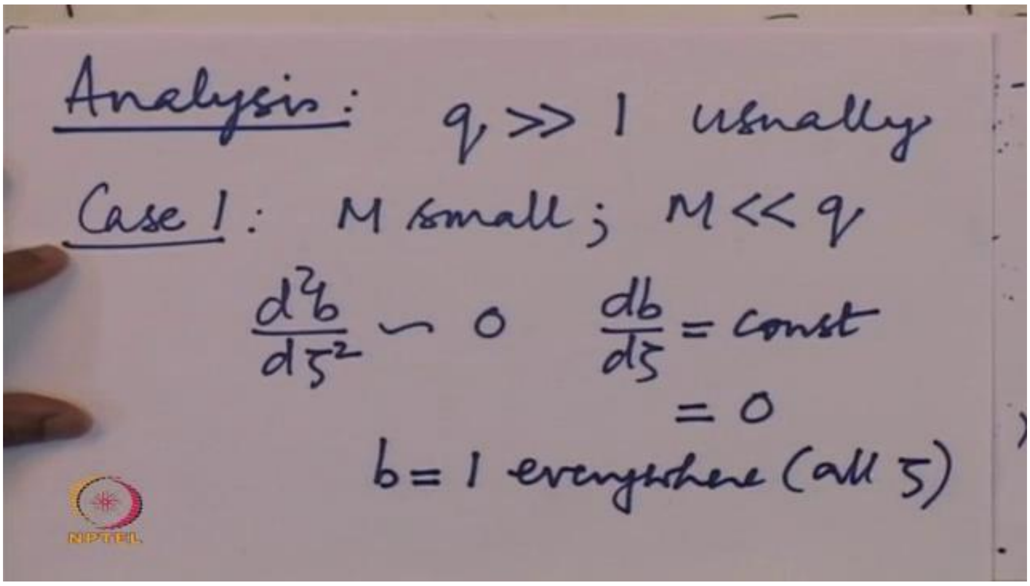
$$\frac{D_A C_A^*}{\delta} \quad \frac{D_B C_{Bb}}{\delta}$$

Relative abu ance

So, we first a note 1 thing that the value of q is almost always much greater than 1 this is, because if you look at the definition of q it has DB and DA; which are similar in magnitude. It has concentration of b which is rather large, b could be if you take an example such as the absorption of Carbon dioxide in solution Monoethanolamine; b would the concentration of Monoethanolamine a in the a q solution that can be very, very large. And CA star is the equilibrium concentration of Carbon dioxide in water and this is usually much smaller than a the concentration of b in the bulk.

So, this is the case for most gastric liquids systems whether you take oxidation reactions in which Oxygen is the gas or hydrogenation reactions in which hydrogenizes gas or gases like Carbon dioxide or H2S or whatever. Usually, the concentration of the gaseous species on the liquid site at equilibrium is a much smaller number as compare to the concentration of the a liquid phase reactant. They that is to say this in this expression the C Bb is almost 100 times or more as compare to CA star. And new once again is a stoichiometric factor which is a small number like 1 or 2 or 3 etcetera.

(Refer Slide Time: 22:45)



Analysis: $q >> 1$ usually

Case 1: M small; $M << q$

$$\frac{d^2 b}{d\zeta^2} \sim 0 \qquad \frac{db}{d\zeta} = const$$
$$= 0$$

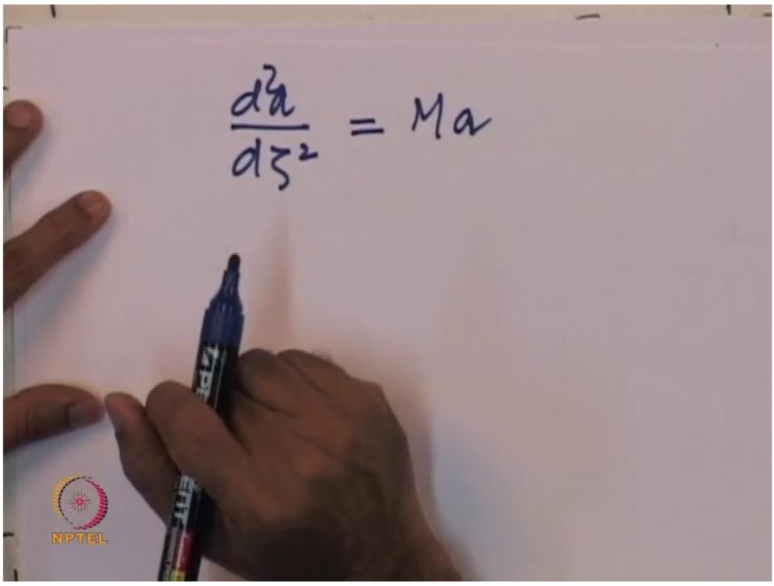
$b = 1$ everywhere (all ζ)

Therefore, the net result is that the value of q is governs by the ratio of C Bb to CA star which is usually very large. So, this can of the order of a 100 even higher and therefore, we make the point that this is usually the case that is q is much smaller than, much greater than 1. So, let us look at reactions in the increasing order of the values of n. In other words, in the increasing order of their relative rate relative to diffusion. Let us first take, the case of M being small in particular we will take the case, where M is much smaller than q; q is a number that is much higher than 1.

So it is not very difficult to find values of M, which are much a less than q. So, if you if this is case looking at the equation for b, where we have the ratio of M to q. And we are saying that M is much less than q we can make the approximation that d squared b upon d zeta squared is approximately equal to 0. Now if this is a case then it means that, db by d zeta is a constant at all values of zeta. We note that zeta is equal to 0 db by d zeta equal to 0 because of the non-volatility condition and therefore, this is equal to 0 everywhere.

So which means, that b is equal to 1 everywhere that is all values of zeta; what we have saying here, is that under these conditions where the value of M is much less than q; what happens is that the concentration of b is uniform throughout the film and bulk concentration privilege write up to the interface.

(Refer Slide Time: 24:54)

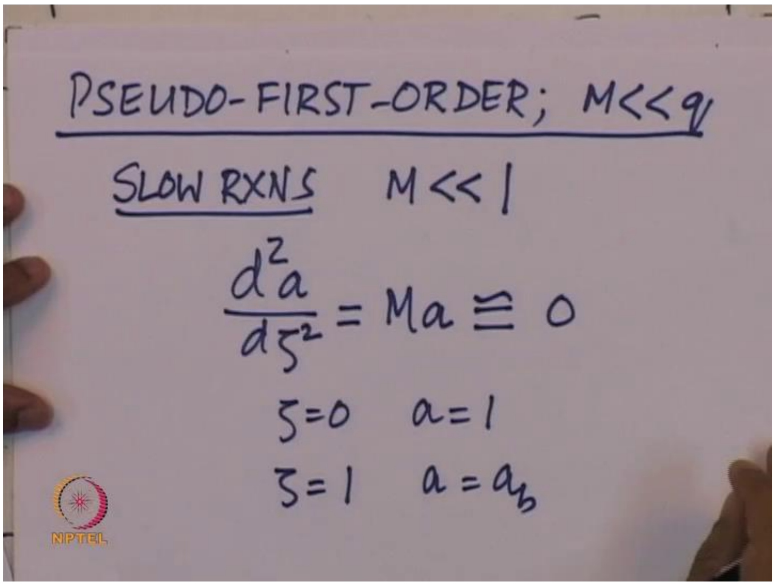


$$\frac{d^2a}{d\zeta^2} = Ma$$

.

So, that is the case looking at the equation for a we immediately have d squared a upon d zeta squared this is the equation that we are looking at and because b is equal to 1 we can write this equation as d squared a upon d zeta squared equals Ma. In other words, this equation has become independent of b and this can be solved by itself. And what we see is the reaction is really behaving like a first order reaction, because the dependence of b does not matter b concentration being constant everywhere.

(Refer Slide Time: 25:42)



PSEUDO-FIRST-ORDER; $M << q$

SLOW RXNS $M << 1$

$$\frac{d^2a}{d\zeta^2} = Ma \cong 0$$

$\zeta = 0 \quad a = 1$

$\zeta = 1 \quad a = a_b$

.

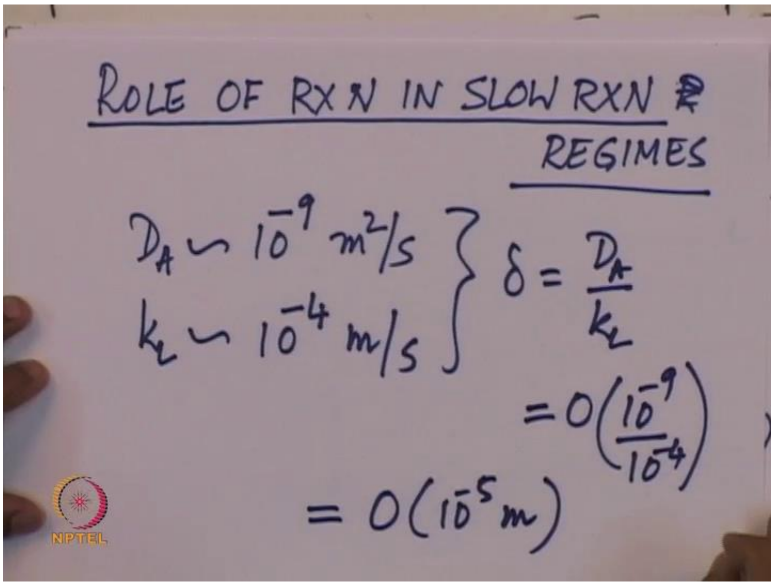
So, this not surprisingly therefore, this conditions that we are considering that is M being much less than q is called as the case of pseudo first order. So, we are going to considering first the reactions for which M is far less than q and these are call the pseudo first order reactions. Under this once again, we will further make the assumption that the reaction is slow enough we will call these as slow reactions for which the value of M is not only much less than q it is much less than 1.

So, this is a more restricted conditions because q as we already remarked is much larger than 1. So, we now demanding that M be not just less than q it must be far less than 1. So, in the equation that we had earlier we had d squared a upon d zeta squared equals Ma for the general pseudo first order regime, so this is very, very small in this case. So, what are we left with, we are left with an equation that is saying d squared a by d zeta squared equal to 0 with the conditions at zeta equal to 0 a is 1 and zeta equal to 1 a is a bulk.

If you look at this, this is no different from the equation that we had written in the a physical mass transfer case; except that in the last lecture we did not non dimensionalzed the equations here we are talking about non-dimensional equations. But this is a exactly the same equation as obtains for the case of physical mass transfer. So what we are saying is, when the reaction is slow enough that the value of M is far less than 1. The reaction really has no effect on the mass transfer process, it is unable to influence the concentration profiles in the diffusion film and the concentration profiles in the diffusion film or govern by the same equation as if there were no reaction. Which means, there the concentration to profile will remain linear.

If the concentration profile remains linear, then the mass transfer coefficient is given by DA divided by delta as in the case of physical mass transfer. And the rate of absorption is exactly same as rate of the absorption in physical absorption case for the same driving force. So, what is that the reaction is doing in this case? As we shall see, the reaction has the important task of actually setting the driving force in this case. So, how do we show this.

(Refer Slide Time: 28:16)



ROLE OF RXN IN SLOW RXN REGIMES

$$\left.\begin{array}{l} D_A \sim 10^{-9}\ m^2/s \\ k_L \sim 10^{-4}\ m/s \end{array}\right\} \delta = \frac{D_A}{k_L} = O\left(\frac{10^{-9}}{10^{-4}}\right) = O(10^{-5}\ m)$$

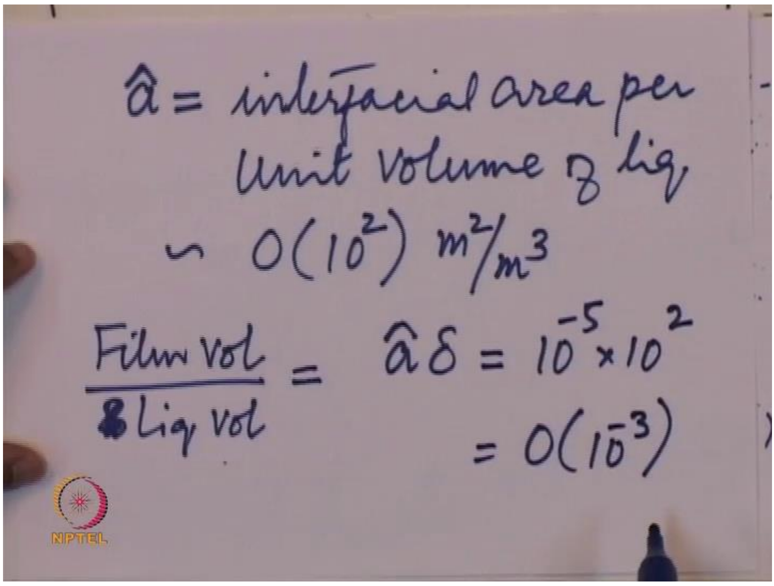
In order to see this we make a balance on the bulk. So, what we are going to consider is the role of reaction in slow reaction regimes these are called as reaction regimes. So, we shall adopts the same nomenclature; the role of reaction is slowly reaction regimes is certainly not to influence the processes in the a diffusion film rather, it is to influence the magnitude of the driving force. How does it do this? We have seen that the reaction is slow enough not to take place to any significant extent within the diffusion film.

So, where is the reaction taking place? The reaction is now taking place outside the film in the bulk of the liquid. So, if we hour to understand the role of reaction we have to draw a balance of the bulk of the liquid and say that, the rate at which a is being transported again to the bulk is equal to the rate at which a is b being consumed by chemical reaction there. And it is this balance that sets the value of the value the concentration of a in the bulk.

Now before we do that, let us take a value of the let us take a look at the typically values of the numbers that we are talking about here. So, we have invoked a diffusivities and these diffusivities usually we have the order of magnitude of above 10 to the power minus 9 meter square per second in SI units. We have talked about, the mass transfer coefficient kL.

So, this usually in process equipment has magnitudes of the order of 10 to the power minus 4 meters per second which means, that the value of delta which is nothing but DA divided by kL in the film theory is of the order of 10 to the power minus 9 divided by 10 to the power minus 4 that is to say, order of 10 to the power minus 5 meters. That is approximately thickness of the film.

(Refer Slide Time: 30:45)



$\hat{a}$ = interfacial area per unit volume of liq

$\sim O(10^2)\ m^2/m^3$

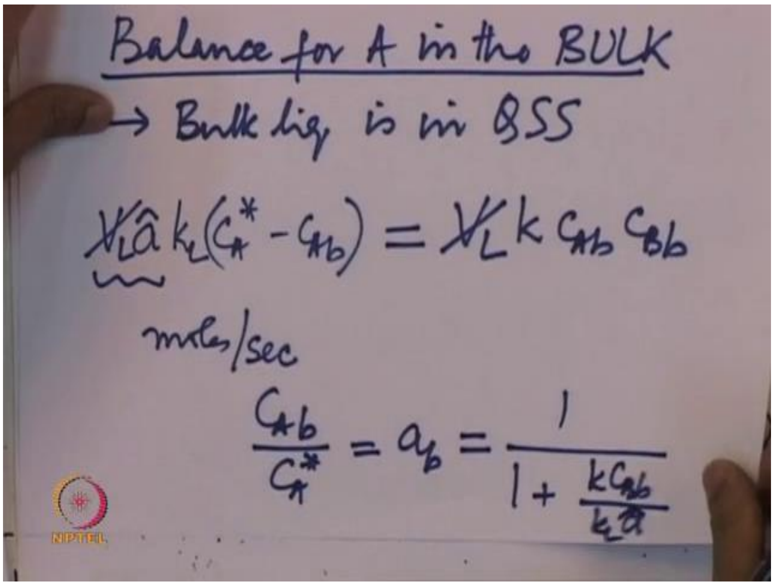
$$\frac{\text{Film vol}}{\text{Liq vol}} = \hat{a}\delta = 10^{-5} \times 10^{2} = O(10^{-3})$$

.

We will also need to defined another quantity this is we call it as a hat and we shall call this as the interfacial area per unit volume of liquid. This in process equipment usually is of order of a few 100 square meters per meter cubed of liquid. So, let us say this is of the order of 10 squared meter squared per meter cube. Now if you look at the this quantity film volume per unit volume of liquid; the volume of liquid that is inside the film as a fraction of total volume of the liquid.

Then this is nothing but a is an interfacial area per unit volume multiplied by delta is the thickness of the film. So, the it is this and this is of the order of the 10 to the power minus 5 multiplied by 10 squared. So, this is of order of 10 to the minus 3, which means that the film volume the volume of liquid within the film is only about 0 1 percent of the total volume of liquid there is. So, when counting the volume of liquid there is in the tank you will be making no significant mistake if you neglect the volume of liquid in the film all together, because that is only about 0 1 percent.

(Refer Slide Time: 32:29)



Balance for A in the BULK

→ Bulk liq is in QSS

$$\underline{V_L \hat{a}}\, k_L (C_A^* - C_{Ab}) = V_L k C_{Ab} C_{Bb}$$

moles/sec

$$\frac{C_{Ab}}{C_A^*} = a_b = \frac{1}{1 + \frac{k C_{Bb}}{k_L \hat{a}}}$$

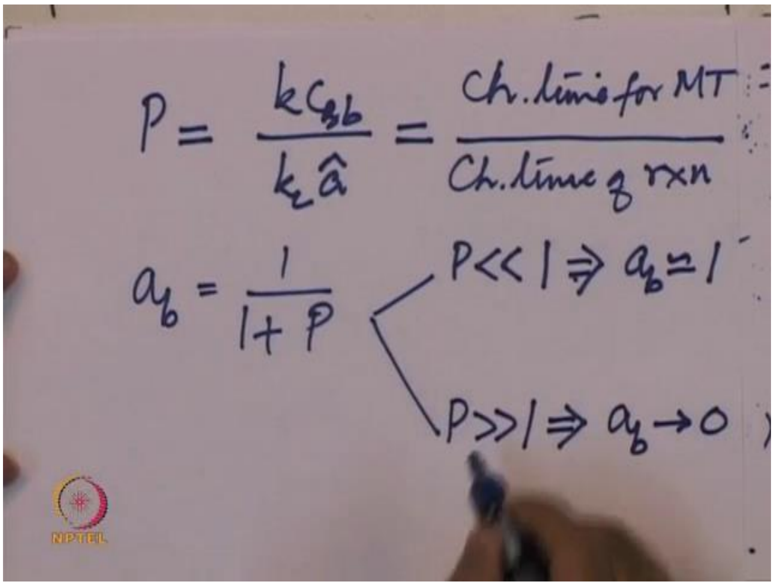
I have made that point let us draw, a balance for A in the bulk. We will assume that, the bulk liquid is in state of Quasi study state. In other words, if concentrations and other conditions are changing in the bilk at all, they are changing sufficiently, slowly with respect to the mass transfer time scales. As transfer as the mass transfer process is concern the conditions in the bulk may be consider to be stationary. Under these conditions the bulk is receiving some amount of A from the film and that amount of A must being consumed by a reaction, because we are not allowing for any accumulation.

Therefore, it is kL multiplied by CA star minus c a b this is the rate of mass transfer a in to the liquid this is multiplied this is per unit area multiplied by a hat VL. So, this is the total amount of area that is present. So, this is the number of moles per second of a that are being transfer from the gas to the liquid; gas to the liquid a at the interface. And since there is no reaction in the a film itself all of this gases being pass into the bulk as well.

So, this must equal the rate at which reaction is taking place in the bulk, which is K times C Ab divided by C Bb per unit volume multiplied by VL. So, this is the equation that governs the state f appears in the liquid bulk. So, VL can be canceled and if you rearrange the equation we have C Ab divided by CA star the quantity that we have called as a b this is equal to 1 divided by 1 plus K C Bb divided by KL a.

So, now we see that there is in additional dimension less group in the works and that is this quantity here. So, as usual we will stop and consider what that means?

(Refer Slide Time: 35:06)



$$P = \frac{k C_{Bb}}{k_L \hat{a}} = \frac{\text{Ch. time for MT}}{\text{Ch. time of rxn}}$$

$$a_b = \frac{1}{1+P}$$

$P << 1 \Rightarrow a_b \simeq 1$

$P >> 1 \Rightarrow a_b \rightarrow 0$

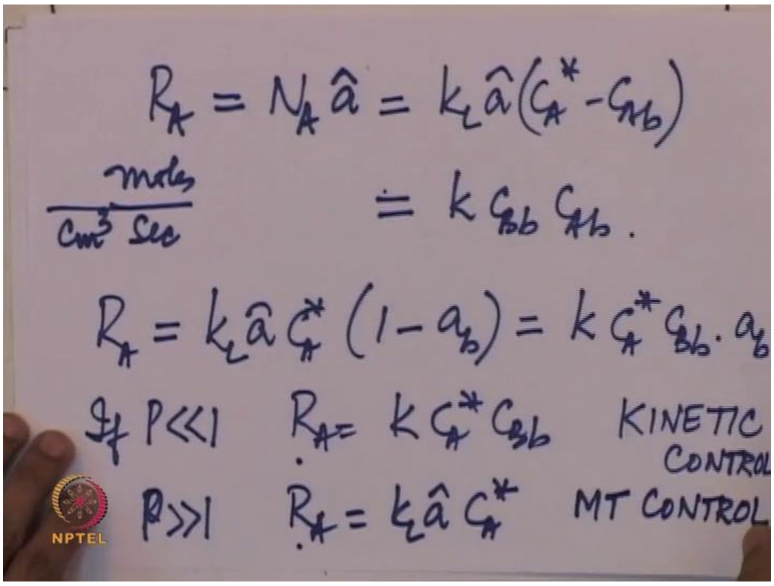
We will call this quantity as P and this is K C Bb divided by KL a notice that both numerator and denominator have units of reciprocal time and therefore, P is once again dimension less K C Bb is the reaction rate constant is a first order reaction rate constant for the second order reaction. Considered, in pseudo first order terms and KL a is the mass transfer rate constant if you like.

So, what this is comparing is the reciprocal rate constant is characteristic time of reaction and reciprocal mass transfer coefficient is characteristic time for mass transfer. So, this quantity P is comparing the rate of mass transfer with the rate of reaction. If the reaction is much faster than the mass transfer process then P has a large value; if reaction is much lower than mass transfer P has a much smaller value.

So, this is P and therefore, we can write this earlier equation as 1 or 1 plus P now this is where the role of reaction present, because the role of the rate of the reaction determines the value of P. And we can imagine 2 extremes situations: 1 in which P is much less than 1 that is the value of reaction a rate is much smaller than the value of mass transfer rate.

In this case, what this equation says is P can be drop from the denominator and this implies ab is almost equal to 1, which means that under these conditions if P is so small then the concentration of a almost attains saturation. The other extreme is P much greater than 1 and under these conditions P will dominate in the denominator, and therefore ab will tend towards to very small values. So, there are these 2 situations now what happens to the rate of absorption in these 2 situations.

(Refer Slide Time: 37:39)



$$R_A = N_A \hat{a} = k_L \hat{a}(C_A^* - C_{Ab})$$

$$\frac{\text{moles}}{\text{cm}^3\ \text{sec}} \qquad \doteq k\, C_{Bb} C_{Ab}.$$

$$R_A = k_L \hat{a} C_A^* (1 - a_b) = k C_A^* C_{Bb} \cdot a_b$$

$\text{If } P \ll 1 \quad R_A = k C_A^* C_{Bb}$ KINETIC CONTROL

$P \gg 1 \quad R_A = k_L \hat{a} C_A^*$ MT CONTROL

The rate of absorption in units of moles per second is nothing but the mass transfer flux multiplied by the interfacial area moles per centimeter cube per second is mass transfer flux multiplied by interfacial area per unit volume and this is given by KL a writing in this equation again. So, this is KL a CA star minus C Ab or the under Quasi study state conditions this is equally equal to k C Bb C Ab.

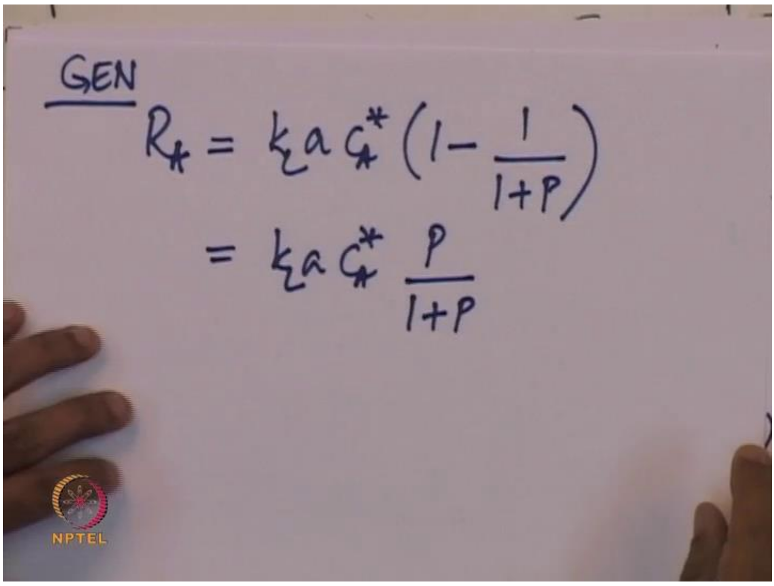
So, this can be written as RA equals kL a CA star into 1 minus ab or these also equal to k CA star C Bb multiplied by ab all right. So, if P is much less than 1 that is this condition here then ab is equal to 1 ab is nearly equal to 1. So, this part of the equation will tell you the mass transfer rate is operating with minimum driving force. So, if you want to calculate the rate using this expression it is not going to be very accurate.

Because, the driving force is so close to 0 that it is difficult to estimate on the other hand, it is very convenient to use this part of this the equation, because ab is close to 1 here. And therefore, RA can be written as k into CA star C Bb. In other words, the rate of absorption is equal to the maximum rate of reaction that you have need expect in the system. Because, this is the concentration of B and this is the maximum allowable concentration of A under the circumstances.

So, the rate of absorption being completely determined by the kinetic rate here, so this would be considered as a case of kinetic control. On other hand, the other extreme of P being much greater than 1 this situation that we talked about ab is equal to 0 or ab is nearly equal to 0 which means, it is not going to be very realistic to calculate the rate from this expression. Because, the reaction driving forces very inaccurately estimated here it is so close to 0 that it is not very easy to measure. And therefore, on the other hand it is very easy to calculate the rate from this expression here.

So, we write RA equal to kL a CA star. Now, if you look at this, this the maximum rate of the mass transfer that is possible in the system. Because, under these conditions the driving force takes the maximum value it can. Therefore, the rate of reaction being completely determine by the rate of mass transfer here this can be considered as a situation of mass transfer control.

(Refer Slide Time: 41:33)



GEN

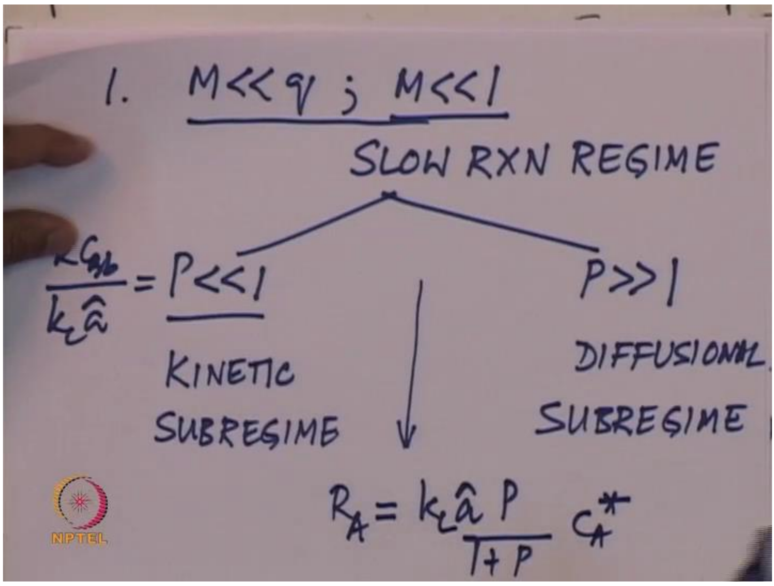
$$R_A = k_L a C_A^* \left(1 - \frac{1}{1+P}\right)$$

$$= k_L a C_A^* \frac{P}{1+P}$$

.

So, let us s what happens in the situation where a P is neither much smaller than 1 nor much greater than 1, in that case we can calculate RA in general we can calculate RA as kL a CA star into 1 minus ab that is 1 by 1 plus P, as we have derived earlier or this is given by kL a CA star multiplied by P times 1 plus P. So, this is how we can calculate the rate of reaction or rate of absorption in the slow regime.

(Refer Slide Time: 42:13)



1. $M \ll q$; $M \ll 1$

SLOW RXN REGIME

$\frac{kC_{Bb}}{k_L \hat{a}} = P \ll 1$

KINETIC SUBREGIME

$P \gg 1$

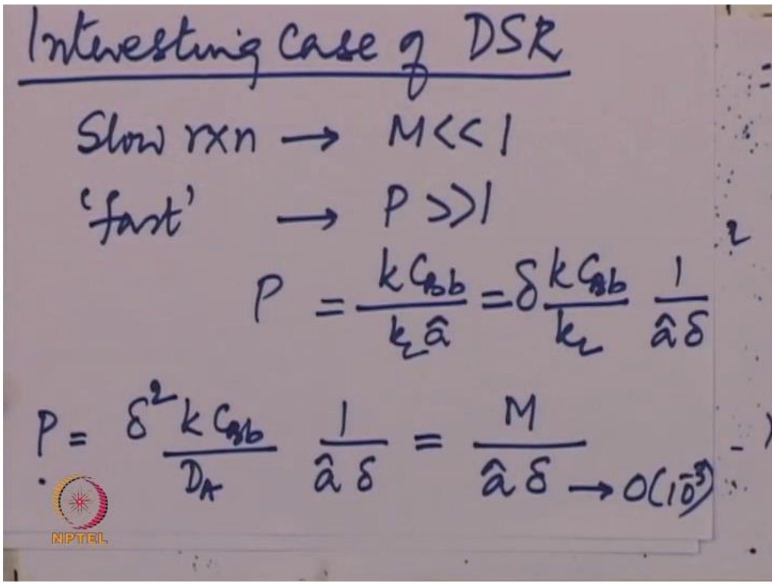
DIFFUSIONAL SUBREGIME

$$R_A = k_L \hat{a} \frac{P}{1+P} C_A^*$$

So, let us get back and then summarize what we have seen so far. So, we have seen the following: first is we are considering cases of M far less than q not only that. Additionally, we consider M far less than 1 and this where calling as the slow reaction regime; under this there are 2 extreme situations there is in additional parameter that comes about P which is nothing but k c Bb divided by kL a P much less than 1 and P much greater than 1. These are the 2 extreme situations and this is called as the kinetic control or we will use the term kinetic subregime and we will the term diffusional subregime for the other extreme, where P is much greater than 1.

Therefore, we have got P much less than 1 is the case where liquid gets saturated, that is the kinetic subregime P much greater than 1 is where the liquid is scarpered of the gas and that is the diffusional subregime. So, we have the pseudo first order regime, under that the slow reaction regime and under that 2 extreme situations: kinetic sub regime and diffusional sub regime. Of course, it is possible for the a value of P to be somewhere in the middle and in that case we have got no particular rate process controlling. And we have got this equation kL a P divided by 1 plus P CA star as giving the rate. Now, before we go to other matters we should examine this case of diffusional subregime in a little more detail, because it is rather interesting.

(Refer Slide Time: 44:32)



Interesting Case of DSR

Slow rxn → $M << 1$

'fast' → $P >> 1$

$$P = \frac{k C_{Bb}}{k_L \hat{a}} = \delta \frac{k C_{Bb}}{k_L} \frac{1}{\hat{a}\delta}$$

$$P = \delta^2 \frac{k C_{Bb}}{D_A} \frac{1}{\hat{a}\delta} = \frac{M}{\hat{a}\delta} \rightarrow O(10^{-3})$$

.

So, we shall call it the interesting case of diffusional subregime why is it interesting? Because, we have on the 1 hand said that the reaction is slow and we have ensured this by saying that M is far less than 1, on the other hand we are saying that the reaction is fast in some sense. Because, we are saying that the value of P is much greater than 1 and P contains the rate constant. Recall, that it is relative to the mass transfer coefficient the value of the rate.

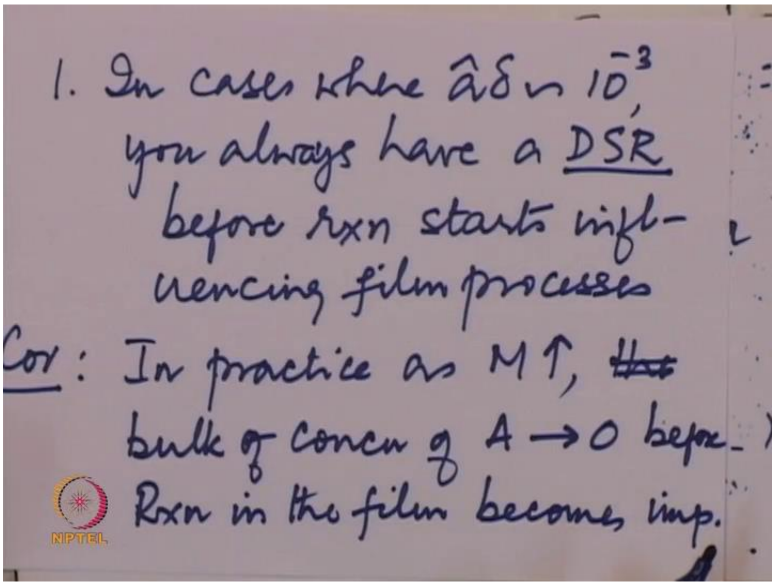
So, is this possible are we talking about 2 opposite things here. Can the reaction on the 1 hand be slow enough ensure that M is much less than 1. On the other hand, at the same time can it be fast to ensure that p is much greater than 1; in order to understand this we examining the definition of P which is this. And we can write this in the following manner: k C Bb divided by kL multiplied by delta there and multiplied by delta here. Now, what is delta divided by kL? So, this is P, so P is delta k C Bb. And kL is nothing but DA divided by delta right a delta.

So, looking at this this is nothing but the value of m divided by a delta. We have already made the point, that this a delta is order of 10 to the power minus 3 in most process equipment. Because, a delta is so small it is possible for a M to be also small and still P to be large. In other words, if M is small, but still much greater than 10 to the power minus 3 P will be large and you will always have a diffusional subregime.

So, as you consider the reactions in order of ever increasing values of M you have a situation where, M is so much less than 1 that is spite of being divided by a quantity of the order of 10 to the power minus 3 P remains much smaller than 1. And then that is when you get the kinetic subregime, as you go to the increasing values of M; M becomes somewhat large that M divided by a delta still is fairly large value.

So, you have M less than 1 and therefore, slow reaction is ensured, but P is much greater than 1. Therefore, the reaction is fast enough compare to the KL a process that the diffusional subregime results. So, because of the circumstance that in most process equipment a delta has this small value of the order of 001 you almost always have a situation of diffusional subregime, before the reaction becomes fast enough to affect the processes in the diffusional film.

(Refer Slide Time: 48:12)



1. In cases where $\hat{a}\delta \sim 10^{-3}$, you always have a DSR before rxn starts influencing film processes

Cor: In practice as M ↑, ~~the~~ bulk of concn of A → 0 before Rxn in the film becomes imp.

.

So, this is a statement of some importance, so what you have said is that, in normal process equipment in cases where a delta is of the order of 10 to the power minus 3, you always have a diffusional subregime before reaction starts influencing film processes. A corollary of this is that what happens in diffusional subregime? In diffusional subregime the concentration of a goes to nearly 0.

So, what we are saying in as a corollary of this statement is that, in practice has you consider reactions of larger and larger values of M or larger and larger velocities. There always or other the bulk concentration bulk concentration of A always goes to 0 before reaction in the film becomes important that is to say so far we have neglecting the occurrence of the reaction in the film.

And remember that we solved the equation d squared a by d zeta squared equal to 0 right. We can continue to do that, as the value of reaction rate increases till the reaction rate is fast enough that the bulk concentration is nearly equal to 0. So, if reaction rate increases beyond this value only, then you need to consider the reaction rate term in the diffusional equation. So, what happens in those cases, we will see in the next class.