Chemical Reaction Engineering

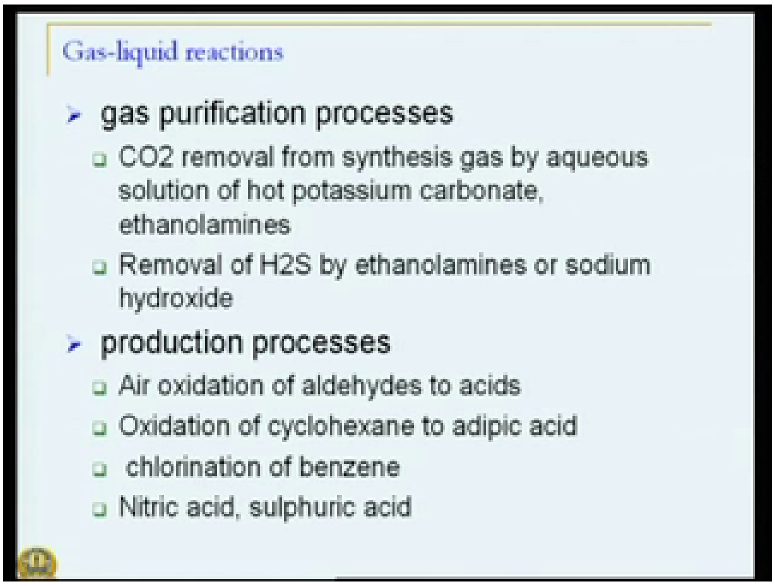
Prof. Jayant Modak
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture No. # 25
Gas-Liquid Reactions

Friends, let us continue our discussion on heterogeneous reactions and in the last session, we discussed about gas solid non-catalytic reactions. Which share a lot of common features with gas-solid catalytic reactions, but the major difference being that non catalytic process are unsteady state processes, that is dynamic in nature, because things are changing with time. Today, we will focus our attention on another class of important heterogeneous reactions, namely gas-liquid reactions.

Now, when it comes to gas-liquid reactions, there are two broad application areas where one encounters these reactions. One is the gas purification processes and these are becoming important not only from the environmental point of view, but quite often when you want to use certain gases for reactions, you do not want any impurities associated with it. You have a gas purification process as an inherent part of any reactor scheme.

(Refer Slide Time: 01:37)



Gas-liquid reactions

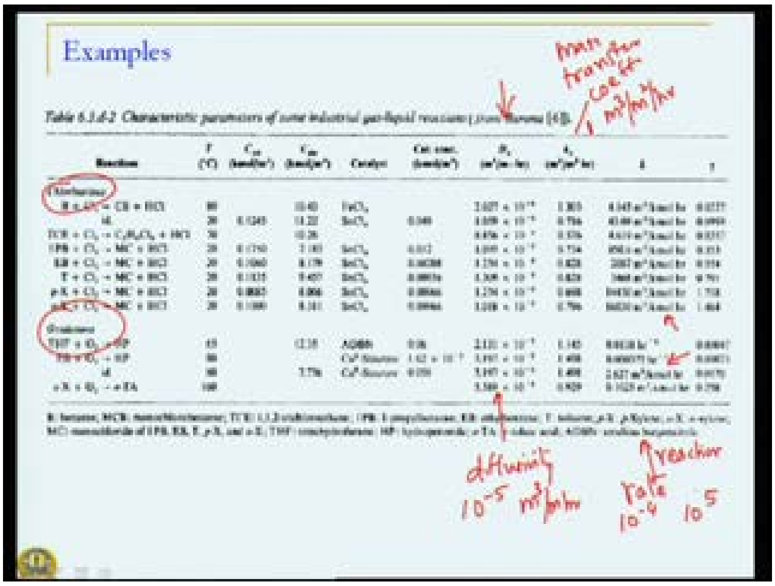
- gas purification processes
  - CO2 removal from synthesis gas by aqueous solution of hot potassium carbonate, ethanolamines
  - Removal of H2S by ethanolamines or sodium hydroxide
- production processes
  - Air oxidation of aldehydes to acids
  - Oxidation of cyclohexane to adipic acid
  - chlorination of benzene
  - Nitric acid, sulphuric acid

We have things like carbon dioxide removal from synthesis gas for example, using aqueous solution of hot ammonia, a hot potassium carbonate or ethanolamines. So, C O 2 removal, essentially it could be in the synthesis gas or it could be in the thermal power plant flue gases from thermal or whichever may be the case. The idea is that you want to remove it in hot potassium carbonate or ethanolamine.

Now, why hot why potassium carbonate? We will talk about it shortly. Then another common polluting agent is sulphur. So, you want to remove it is hydrogen sulphide, again by sodium hydroxide or reacting ethanolamines and so on. So, these broad classes of reactions you can say that they are more of a purification step than any production step. That is not to say that these are not important, they are important in their own right, but you are not getting a definite product out of these reactions.

The production processes where gas-liquid reaction occur, on the other hand as a target product. For example, air oxidation of aldehydes to acids or oxidation of cyclohexane to atopic acid, which is an important monomer. Chlorination of benzene formation of or production of nitric acid, sulphuric acid and so on. Where product namely acids or chlorobenzenes or sulphuric acid, these are important products which we want to manufacture using gas-liquid reactions.

(Refer Slide Time: 03:36)



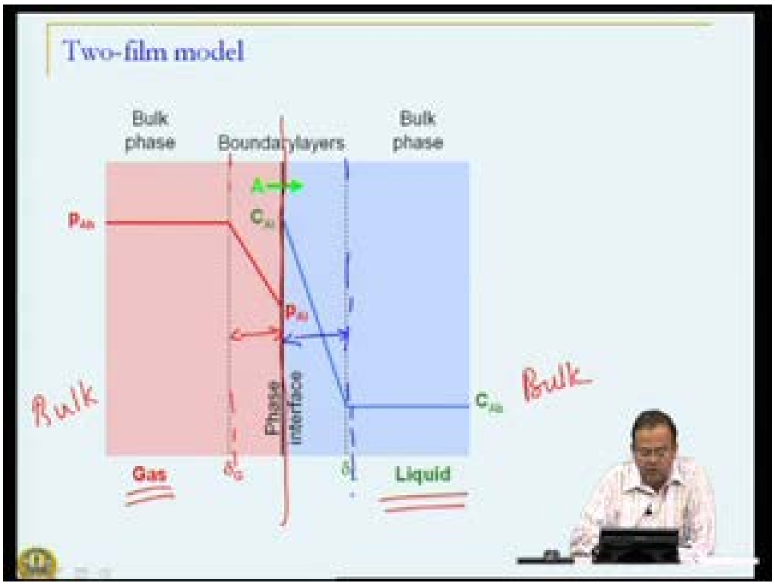
Examples

Now, gas-liquid reactions. Before we embark on various different types, let me just highlight and I understand you would not be able to see much here. Let me just read it out the message I want to convey here. Here are various different reactions such as chlorination reactions or different oxidation reaction, so large number of reactions. Their working temperatures anywhere between 20 to 100 degrees centigrade depending on, of course the boiling point of the liquid under consideration, typical catalyst and so on. But what I want you to draw your attention are to this column, which talks about the diffusivity of the component, which is in the order of 10 raise to minus 5 meter cube per meter per hour, diffusivity of various gases.

The second column over here is the mass transfer coefficient mass transfer coefficient, which is again in meter cube per meter square per hour and is in the range of 0.5 to 1. I mean order of magnitude, if I were to say, I would say it is about 1 meter cube per meter square per hour. But what I want to now focus on is this reaction rate constant for various different reactions. This reaction rate constant actually is having a magnitude, for example, as low as 3 into 10 raise to minus 4, for some oxidation ethyl benzene oxidation reaction, to as high as chlorination of Roth xylem which is 1.6 into 10 raise to 4.

What therefore, I am implying is that reaction rate can be varying from 10 raise to 4 to 10 raise to minus 4 to 10 raise to 5. That is while diffusion of gaseous component, the mass transfer coefficient is more or less of the same order of magnitude. There is a wide variation in the order of magnitude of the chemical reaction. Now, if you look at the reaction such as chlorination of mono chloral benzene and the reaction. Compare that reaction with oxidation reaction, the reaction rate is almost infinitely large from 10 raise to minus 4 to 10 raise to 5. So, 10 raise to 5 is almost infinitely larger compared to 10 raise to minus 4. While discussing gas-liquid reactions and trying to visualize how these reactions take place. We have to use different strategies depending upon what is the kinetics of the process. We will do that one by one, saying that a reaction is slow or moderate or instantaneous and so on.

(Refer Slide Time: 07:25)

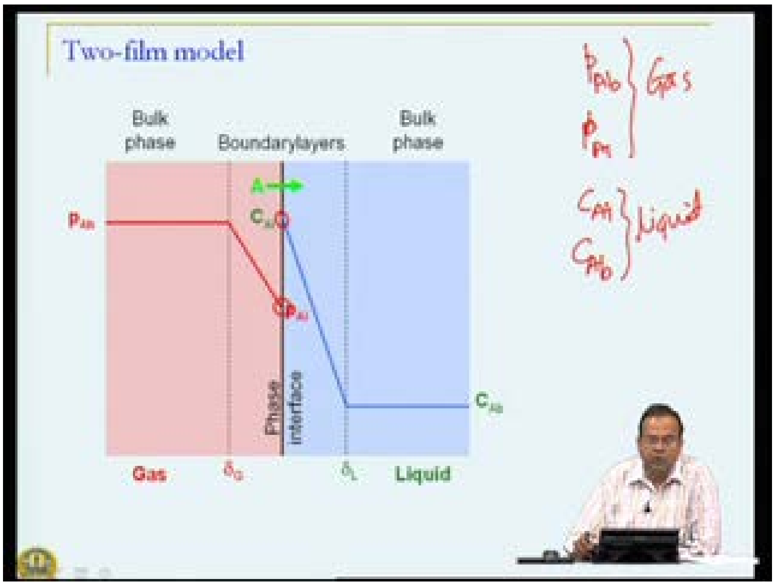

Two-film model

But let us look at the broad framework under which these reactions are often looked at. And this broad framework is that of a two-film model. So, what we have here is, let us say that we have a reaction between a and b, but even before we come to the reaction of a and b that is, a is a gaseous component, b is a liquid component. Let us try to look at what will happen when gas and liquid are brought in contact with each other. And that forms the basis of two-film theory.

Let us say we have a gas on the left hand side, which is in contact with the liquid and there is an interface, which distinguishes between the gas and liquids. So, that is a phase interface. We have bulk gas, we have bulk liquid and they are in contact with each other. Now film theory assumes that, all the resistance to mass transfer is located in a thin film surrounding the interface. So, on the gas side we have one film and equal equivalent film on the liquid side as well. All our mass transfer resistance is located in these films. For example, this one for liquid, having length delta l and this for gas, having length delta g. So, beyond these two boundaries, both on gas side and liquid side, there is a uniformity of concentration. That is how film theory views gas-liquid mass transfer.

We have gas that is component A in the gaseous phase, and let us say it is partial pressure is P A B, B denoting bulk. So, the concentration of partial pressure is uniform till the boundary, but then, that concentration decreases, because of mass transfer resistance. And at the interface it is P A i. So, P A B is in the bulk and P A i is at the interface. So, this is from the gas side.

(Refer Slide Time: 09:55)

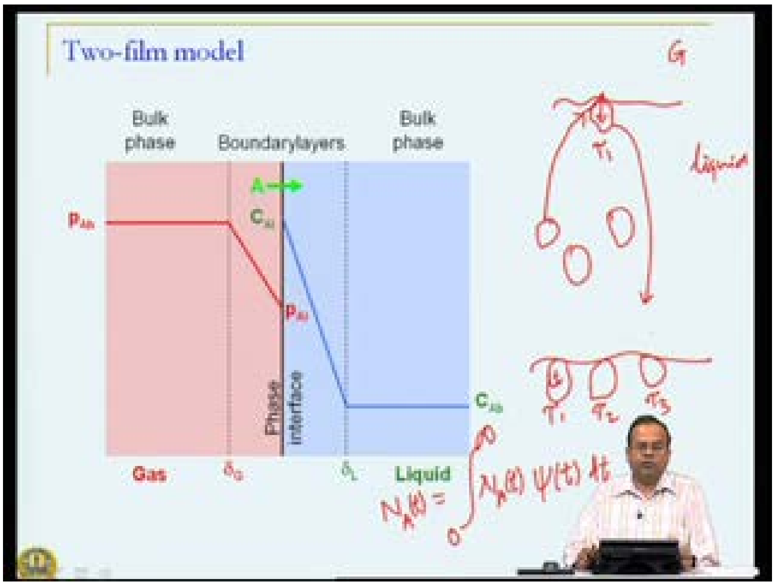


Two-film model

Now, at the interface there is equilibrium between the gas and it is liquid. At the interface the concentration of A in the liquid is C A I, which is in equilibrium with partial pressure P A I, equilibrium being described by Henry’s law and so on. And then again because of resistance, the concentration decreases and at the interface it reaches a value C A B. And so the concentration of a in the bulk liquid is C A B. So, this is my liquid side.

Now, what film theory assumes is that these profiles are established almost instantaneously. The interface has no capacity to store mass. So, steady state is instantaneously reached and essentially this is a steady state model. Now, one may argue the validity of such assumptions, but it turns out that this is workable theory. It has provided satisfactory answers to many experimentally observed phenomena. But an essentially captures the essence of the process, even though there are quite a few more sophisticated theories. For example, there are whole bunches of, what we call surface renewal theories, which or penetration theories. Which view this whole phenomenon in a slightly different light. We would not spend the whole lot of time, but let me give you the background for looking at these kinds of processes.

(Refer Slide Time: 12:22)



Two-film model

$$N_A(t) = \int_0^\infty N_A(t)\,\psi(t)\,dt$$

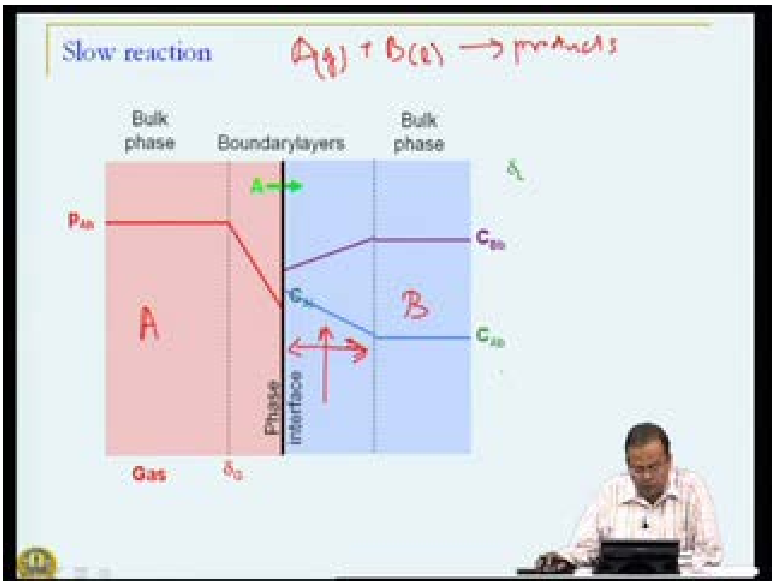
So, what for example, surface renewal or penetration theory says is that, there is a interface there is a gas, there is a liquid, but then the theory or the theory in which as this gas liquid mass transfer in a following manner. This is the bulk liquid, which composed or consist of let us say various fluid element. So, this fluid element comes to the gas interface stays for their sometime, let us says tau 1 and then goes back to the liquid. The fluid element which will have component liquid reacting component, comes to the surface there is a exchange of material or gas and liquid stays here on this surface for certain amount of time, tau one let us say. And then goes back in the bulk and this process continues forever.

If you look at gas-liquid interface at any given point of time, there will be different fluid elements having edges tau 1, tau 2, and tau 3. That is they have spent that much amount of time at the interface, before they actually go back. These fluid elements have capacity to store mass. So, these are basically unsteady state processes. Now, the fluid elements are continuously replaced that is this fluid element once it comes does not remain there forever. They are replaced by other fluid elements, depending upon the hydrodynamics of this bulk liquid. Now, there are various different theories, which say that all fluid elements, some theory says that all fluid elements have same age, so they all spend time equal to tau 1. Some say that there is a distribution, so psi of t, D t is the distribution of age and if N A of t that is, if the fluid element has spent time t here, the rate of absorption of gas into liquid is N A, then integrated over all possible residence times is my rate of reaction or the average value of flux.

There are various different approaches. Now as I say it turns out that, whether you use this penetration theory, surface renewal theories, that prediction difference in prediction of to these two models, even though they are fundamentally different is hardly few percentage point. In fact, that most common only in the transition rate, at the limits the behavior is pretty much pretty much same. These are more realistic penetration theories, but computationally or mathematically little difficult to handle. Film theory, conceptually little weak, but elegantly any simple terms describe the entire process. It is not surprising that film theory has been extensively used to look at gas-solid reactions.

So, now let us go back to our earlier observation that different reactions have different reaction rates. Let us say that we have a very slow reaction. The reaction is very slow, so much so.

(Refer Slide Time: 16:27)



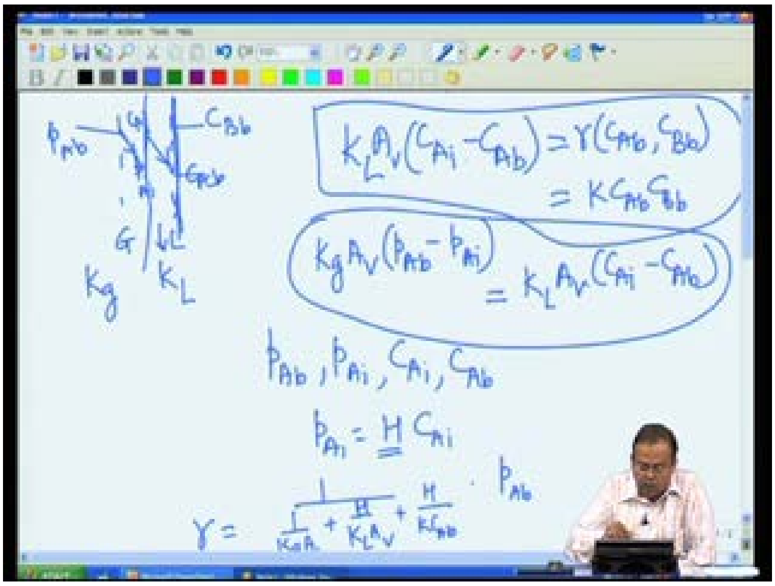
Slow reaction

$A(g) + B(l) \rightarrow$ products

Now, let us say our reaction is of this type, A in the gas component reacts with B in the liquid component to give rise to certain products. So, that is our reaction in short. We have our gas A on the gas side we have B on the liquid side. Once again the film theories C A i P A i and so on. But what we are essentially saying is that reaction rate is so low. That there is hardly any reaction in the film and most of the reaction is in the in the bulk liquid. So, that there is very little reaction over here in this range. Where is only diffusion, because reaction is so slow compared to diffusion there is hardly any reaction in the bulk liquid, reaction is only in the sorry hardly any reaction in the boundary layer, but entire reaction is in the bulk liquid.

Let us let us try to look at how do we handle this kind of reaction. If we try to write down the mass balance for this situation, it would look something like this.

(Refer Slide Time: 18:08)



$$k_L A_v (C_{Ai} - C_{Ab}) = r(C_{Ab}, C_{Bb}) = k C_{Ab} C_{Bb}$$

$$k_g A_v (p_{Ab} - p_{Ai}) = k_L A_v (C_{Ai} - C_{Ab})$$

$p_{Ab}, p_{Ai}, C_{Ai}, C_{Ab}$

$p_{Ai} = \underline{\underline{H}} C_{Ai}$

$$r = \frac{1}{\frac{1}{k_g A} + \frac{H}{k_L A_v} + \frac{H}{k C_{Bb}}} \cdot p_{Ab}$$

We have our, let us say our liquid side film, gas side film, pressure P A b, pressure P A i here, concentration C A i and C A B over here. So, pressure is decreasing, bulk decreasing, concentration decreasing and then there is a reaction in the in the bulk. That is how we visualize these slow reactions to slow reactions to proceed.

Let us try to write down now mass balance equations. Remember this is a steady state process, so no accumulation whatever is coming at the interface is going to the liquid and so on. Let us say that our liquid side mass transfer coefficient is K L. That is an idea basic idea of film theory that is we characterize these two boundary layers gas side and liquid side by their respective mass transfer coefficients K g and K L. Let us say K L is the liquid side mass transfer coefficient and if we focus on this particular boundary. So, let us try to, now look at what is happening at this particular boundary. There is a transfer of mass from the interface to the boundary that is delta l. So, let us try to characterize that mass transfer by K L and the flux given will be C A i the driving force minus C A b.

So, this will be flux driving force into mass transfer coefficient, but we want per unit volume. So, let us say that A V is the area of this interface per unit volume of the liquid. So, K L A V into C A i minus C b must be equal to, what is happening at these interface? The reaction so that must be equal to the rate at which the reaction is occurring.

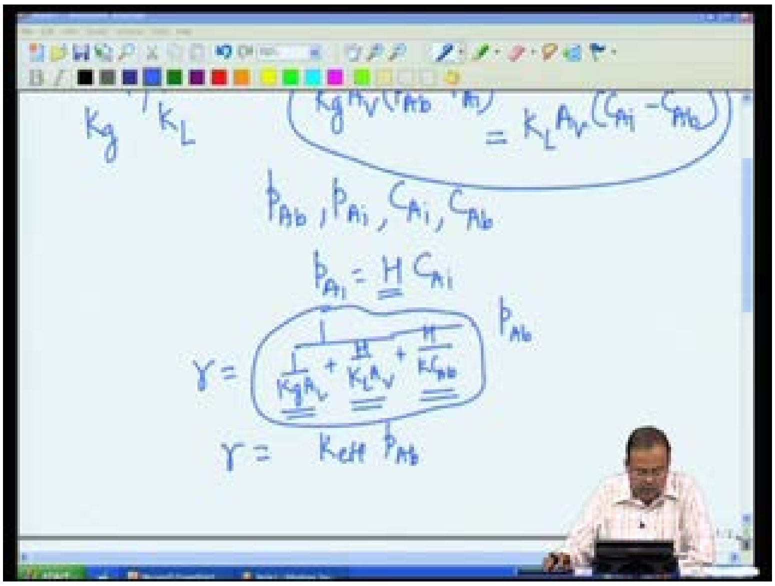
Let's say the reaction is occurring at a rate r, which depends on the concentration of A in the bulk and C in b in the bulk. And let us say that concentration is K into C A b into C B b, law of mass action kinetics let us say. So, that is as far as the liquid side is concerned. Now, what is happening on the on the gaseous side, the same that is the mass which is coming from the bulk of the gas to the interface, must be the mass which is transferred from the interface to the liquid. So, K g into A V, which is the mass transfer coefficient from the gas side into the interfacial area. Multiplied by the driving force P A b minus P A i must be equal to the rate at which the component A is moving in the liquid. All we are saying is that at this particular interface, there is no an accumulation. So, whatever is coming from here, the rate of transfer is same as what is going inside.

So, we have now in this relationship. So, we have basically two relationships, one what is happening at the bulk liquid and another one which is happening at the interface. In which we notice that we have concentration of A in the bulk phase, partial pressure of A at the interface, concentration of A at the interface and concentration of A as well as B in the bulk.

Bulk quantity is a something that we can actually measure; we can know what in the partial pressure in the gas phase. We can actually measure what is a concentration in the bulk. Interface is something that we do not know. So, what can be done? However, is one more assumption that is at the interface the gas is in equilibrium with the liquid. That means, the concentration of A at the gas phase P A i is in equilibrium, which we can express it using Henry's law and Henry's constant equal to h into C A i. This is something what gives us the solubility for example, the equilibrium composition.

So, composition of oxygen in equilibrium with water. What is the concentration of oxygen in water? That is roughly about 8pp.So, this is that Henry's constant h. we bring that in, and if we now use this three relationships, namely this two relationships and this equilibrium. we can write actually the rate of reaction as 1 by 1 by K g A v plus 1 by 1 by K L A v H by K L A v plus H by K C A Z into partial pressure of A b. Or in other words, using three relationships, we can eliminate 3 of the 4 unknowns and write the rate in terms of terms of bulk property.

(Refer Slide Time: 25:03)



K_g, K_L

$K_g A_v (p_{Ab} - p_{Ai}) = K_L A_v (C_{Ai} - C_{Ab})$

$p_{Ab}, p_{Ai}, C_{Ai}, C_{Ab}$

$p_{Ai} = \underline{\underline{H}} C_{Ai}$

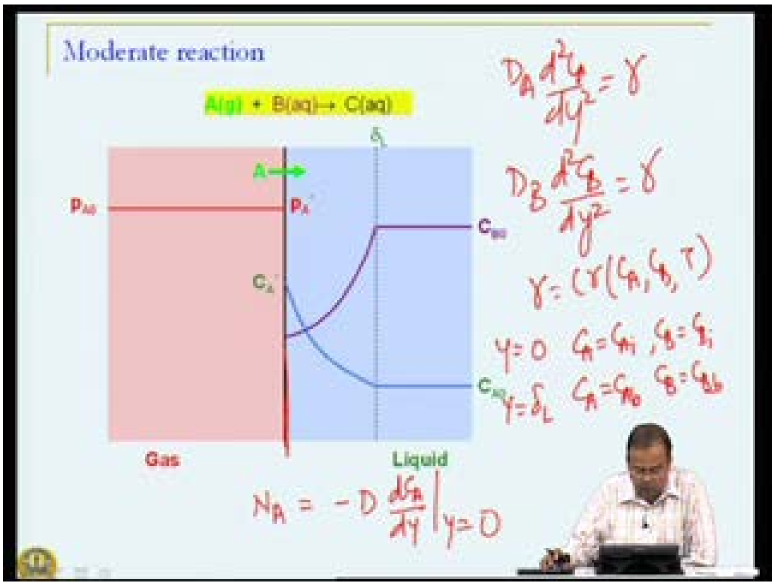
$$r = \boxed{\frac{1}{\underline{\underline{\frac{1}{K_g A_v}}} + \underline{\underline{\frac{H}{K_L A_v}}} + \underline{\underline{\frac{H}{k C_{Ab}}}}}} p_{Ab}$$

$r = K_{eff} p_{Ab}$

So, this one for example, this one for example, this whole thing is under, this one for example, tells us that this is now my equivalent rate constant, which is not essentially same as the kinetic rate constant. But this is how. So, let us say we can say this as k effective into partial pressure of A B that is my rate.

And if you look at this particular effective rate, you can immediately see a relationship which is reminiscent of resistances in series. There are three processes transfer from gas to the interface, from interface to the liquid and then reaction in the bulk liquid. So, these three processes are represented by their respective resistances in series. And coefficient is one over resistance. So, that is how we get our effective rate constant or effective coefficient transfer coefficient, which now is determined by not only the mass transfer coefficient, but the reaction rate as well. This is how we can deal with a very slow reaction. Essentially saying that, there is no reaction in the film, but reaction is mainly confined to the bulk liquid.

(Refer Slide Time: 26:37)



Moderate reaction

$A(g) + B(aq) \rightarrow C(aq)$

$$D_A \frac{d^2 C_A}{dy^2} = \gamma$$

$$D_B \frac{d^2 C_B}{dy^2} = \gamma$$

$$\gamma = (\gamma(C_A, C_B, T)$$

$$y=0 \quad C_A = C_{Ai}, C_B = C_{Bi}$$

$$y=\delta_L \quad C_A = C_{Ab} \quad C_B = C_{Bb}$$

$$N_A = -D \frac{dC_A}{dy}\Big|_{y=0}$$

Now, let us make these reaction little moderate. Again, we are looking at the same reaction A component from the gas reacts with B component, which is in the liquid phase or aqueous phase and gives rise to certain product. We keep our basic theory same as same as before film theory and do a slight modification in this particular scenario. Namely, let us not worry so much about bulk concentration. That is gas side mass transfer resistance, we will keep it aside for a time being, and when time comes will bring it back. What is an essence of this? So, what we saying is now reaction rate is moderately high.

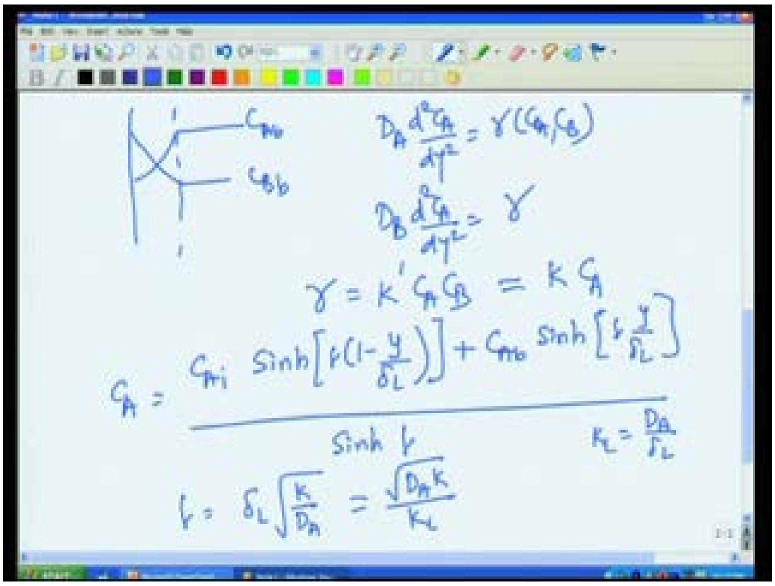
Which implies that there is a reaction in the bulk liquid as well as reaction in the film itself, the liquid side. Gas side there is no possibility of liquid, because one of the important assumptions in all this is, that liquid component is fairly non-volatile. So, reaction does not occur between A in the gas and equivalent B in the gas. The reaction is actually A in the gas, which goes to A as a liquid component and then there is a reaction. And we are discussing, whether that reaction is taking place. Where is that reaction taking place? For slow reaction in the film there is no reaction, only in the bulk. But, when it comes to moderate reactions, that is reactions which are little faster, there is a possibility that reaction can reaction can take place in the bulk as well as in the in the film.

So, what is happening in the film? Essentially, we have diffusion of A and reaction and similar story for component B as well. We can once again analyze this by writing diffusion reaction equation, which we had already done for gas solid catalytic and non-catalytic reactions. If we say that D A is the diffusivity of A in this film. So, D in this film, liquid side film what is happening in the liquid side film, what we have is diffusion of A.

Let us call this as y equal to 0 and this as y equal to delta l. So, we are trying to see what is happening between y equal to 0 and y equal to delta l. let us look at what is happening in the film? What is happening in the film is, we have diffusion of A which we can describe by this diffusion equation some rate of reaction and equivalent relationship for B, because we have two components. So, diffusion reaction equation, where these rate is a function of C A, C B, and temperature and so on.

We have this reaction which is going on. and what are the boundary conditions at y equal to 0, concentration of a is C A I, concentration of b is C b i. Let us say, we do not know what that concentration is, but let us leave it in terms of C A i and C A b and C B i and C B b. That is the bulk concentration and the individual concentration. So, these are my boundary conditions. Now, how do we get C A b and C B b and so on? So now, if we look at the flux in A as visualized at these interface that is what is the rate of overall phenomena. As if we visualize this in this interface, because that is the rate at which A is getting depleted from the bulk liquid and that is what ultimately matters. That is what the rate of reaction would be. So, this would be simply minus D d c A D y at y equal to 0. So that is what will tell me, what the rate of reaction? So, let us take this little further and see what is what is happening over here.

(Refer Slide Time: 32:23)



$$D_A \frac{d^2 C_A}{dy^2} = r(C_A, C_B)$$

$$D_B \frac{d^2 C_A}{dy^2} = r$$

$$r = k' C_A C_B = k C_A$$

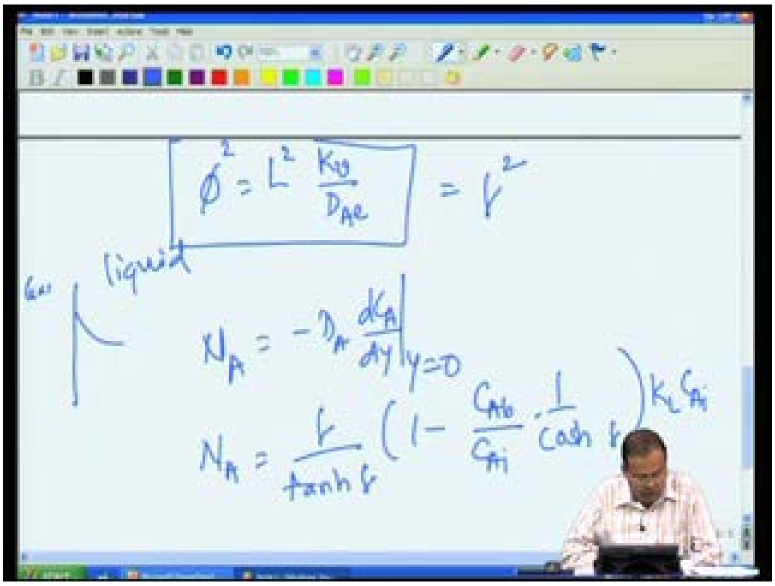
$$C_A = \frac{C_{Ai} \sinh\left[\gamma\left(1 - \frac{y}{\delta_L}\right)\right] + C_{Ab} \sinh\left[\gamma \frac{y}{\delta_L}\right]}{\sinh \gamma} \qquad k_L = \frac{D_A}{\delta_L}$$

$$\gamma = \delta_L \sqrt{\frac{k}{D_A}} = \frac{\sqrt{D_A k}}{k_L}$$

So, what we are now looking at is gas liquid interface, the liquid side boundary, diffusion of A and B and the reaction at concentration. Whatever, the bulk concentration and intermediate concentration is. We had written the equation of diffusion D A d square C A d y square equal to r of C A and C B, let us say. Similarly, D B d square C A d y square equal to r and then corresponding boundary conditions. And we can now solve these equations, if the kinetics is such that reaction rate is K prime C A C B. and if you say that the liquid concentrations are generally much higher than gas. So, they do not change much. So, the equivalently represent it as a first order reaction in concentration of A. Then what we will get is a pseudo first order reaction in terms of A. and if we now plug this into this particular equation, mass balances. We can actually solve, what is the concentration of A and it turns out this can be expressed it is slightly involved expression. That is concentration of A as a function of distance divided by sine gamma.

Where gamma is delta l root of K by D A, K is the kinetic rate constant, D A is the diffusivity delta l is the thickness. Since, in the diffusion theory your mass transfer coefficient K i is D A by delta l, this can be also equivalently written as root D A K divided by K L. That is another way of writing the same thing. Since we defined mass transfer coefficient it comes out as ratio of diffusivity by film thickness.

(Refer Slide Time: 35:27)



$$\boxed{\phi^2 = L^2 \frac{K_v}{D_{Ae}}} = \gamma^2$$

$$N_A = -D_A \frac{dC_A}{dy}\Big|_{y=0}$$

$$N_A = \frac{\gamma}{\tanh \gamma}\left(1 - \frac{C_{Ab}}{C_{Ai}} \cdot \frac{1}{\cosh \gamma}\right) k_L C_{Ai}$$

Now, let us look at this parameter little bit and try to see what it is trying to tell us. If you look at this parameter is actually referred to as hatta number, H a or sometimes just H. now, what is it trying to trying to tell us. If you look at actually this particular form you have seen this particular form, when we define Thiele modulus for gas solid reactions. For example, we define Thiele modulus or phi square, as if it was a slab geometry l square reaction rate constant K v by diffusivity D A e, which actually in some way same as the square of this parameter gamma that we have.

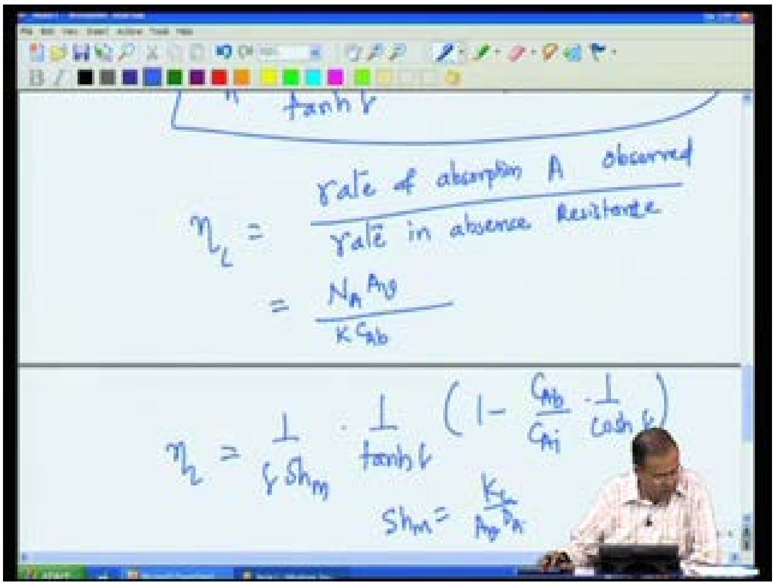
What is hatta number? It is equivalent to Thiele modulus, but for historical reasons, it is referred to as hatter number in honor of scientist, who first observed it for gas liquid reactions. It is trying to tell us that this number is actually rating two different phenomena diffusion and reaction. And we can argue in the same manner, as before that it is a ratio of time scale for diffusion to time scale for reaction. And therefore, a small value of gamma or large value of gamma has a similar significance, as small or large value of Thiele modulus, because they are actually representing ratio between diffusion and reaction.

So now, using this particular value of C A and as I said earlier that, if we are positioned in the gas phase, the rate of disappearance of component A from the gas phase, is nothing but the flux in A of C A at y equal to 0. So, if you have positioned yourself in the gas, all this is seeing is that there is certain finite flux in the liquid.

Whether, there a reaction or what rate that reaction is occurring is not experienced by the gas, but because it is a steady state theory, whatever is the rate of disappearance or overall rate of reaction must be the same as rate of disappearance from the (( )). So, if we now use our solutions for N A, we actually get N A equal to gamma by tan gamma into 1 minus C A b by C A i 1 by cos gamma into K L into C A i.

So, now we have gas liquid reaction, which again, so this is my rate of rate of reaction. This is what I will observe the rate of disappearance of C A from... So now, I can once again look at this rating in the following manner. Because there is a mass transfer and reaction, I know my reaction rates are generally lower, particularly when we have a first order reaction. We saw also situation where reaction rates actually may be higher, but that was a case of non-isothermal reaction pellet and so on.

(Refer Slide Time: 39:27)



$$\eta_L = \frac{\text{rate of absorption A observed}}{\text{rate in absence Resistance}}$$

$$= \frac{N_A A_v}{k C_{Ab}}$$

$$\eta_L = \frac{1}{\gamma Sh_m} \cdot \frac{1}{\tanh\gamma}\left(1 - \frac{C_{Ab}}{C_{Ai}} \cdot \frac{1}{\cosh\gamma}\right)$$

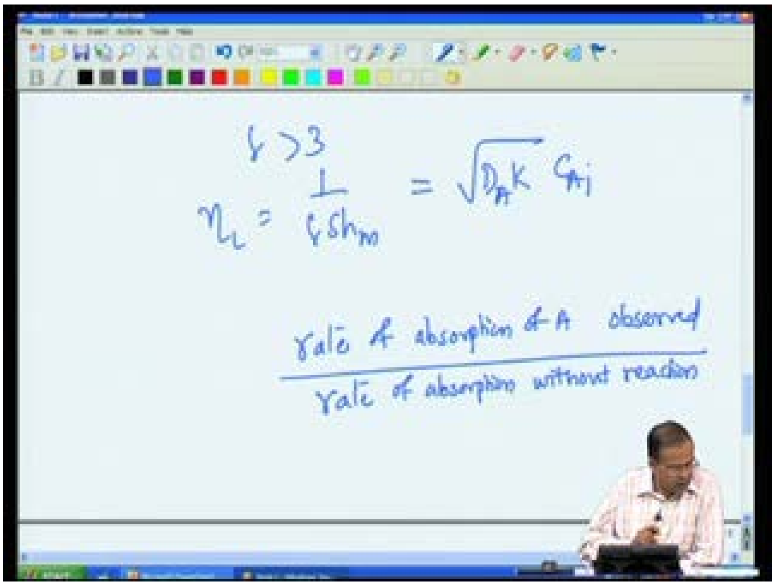
$$Sh_m = \frac{k_L}{A_v D_A}$$

So, I can now define a rating parameter, eta l let us say. Which is rate of disappearance of A actually observed. And I am going to; I do not like this word disappearance. So, I am going to say rate of absorption of A in the liquid. whether you call disappearance from the gas phase or appearance in the liquid is a shame. So, rate of absorption of A observed divided by the rate that would be there in absence of mass transfer resistance. And what will be this rating parameter, the actual observed is N A into A V, we express in terms of unit volume. And what would have been the rate; if mass transfer resistance was not there the rate would have been our kinetic rate k into C A b.

So now, I can now take this N A look at this effectiveness factor or rating parameter. And write it equivalently in the following form. So, this would actually work out to be eta l as 1 over gamma into Sherwood number for mass transfer into cos gamma. So, this is very much similar to our effectiveness factor idea that is you will get actually almost very similar result. If by the way Sherwood number for mass transfer here is K L by a b into D A.

You will get the same result that is; if gamma is small then this effectiveness factor is close to unity. Indicating that diffusion resistances have no role to play diffusion processes are fairly fast and therefore, we get the same result.

(Refer Slide Time: 42:16)



$$\gamma > 3$$

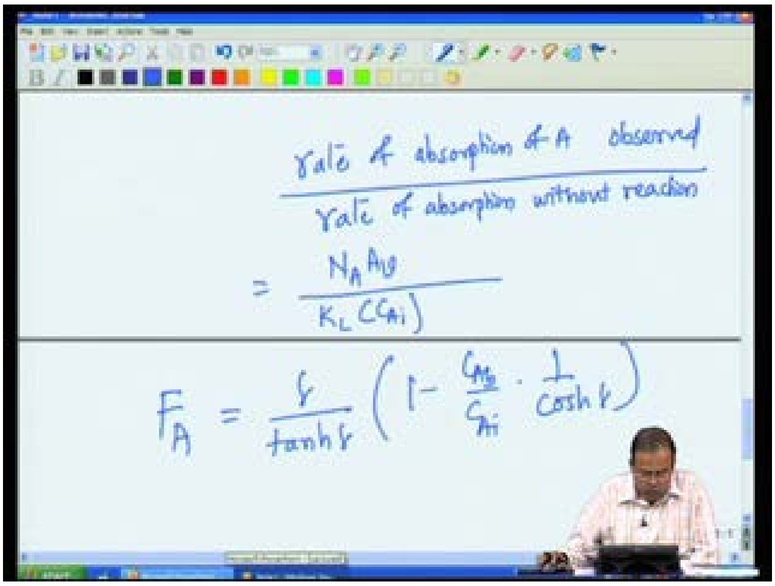
$$\eta_L = \frac{1}{\gamma Sh_m} = \sqrt{D_A k}\, C_{Ai}$$

$$\frac{\text{rate of absorption of A observed}}{\text{rate of absorption without reaction}}$$

Now, this is again one can argue that when gamma is greater than 3. For example, your cos gamma value is greater than 10 and C A b by C A i is close to 0. And therefore, eta one for example, works out to be 1 by gamma into Sherwood number for mass transfer or if you put everything back together, this will work out to be D A K into C A i. it is independent of K L and so on. Now, what happens if you try to look at this process in a slightly different manner? That is what we are saying is that the gas is getting absorbed in the liquid, but what is a role that reaction plays into this. So, I can rate this whole process in a slightly different manner saying that let me look at the observed rate of absorption. So, same as before rate of absorption of A observed. And earlier, I rated it with what would have been rate, if mass transfer resistance was not there. But now, let me rate it with what would be the rate of absorption, if reaction was not there.

Instead of saying that mass transfer has reduced my reaction rate, let me try to see what has happened to the observed absorption rate. Because of reaction, that is compare it with what would have happened, if reaction was not there. And this factor once again, we can use the same relationships and it turns out that factor is tan gamma by gamma 1 minus C A b by…

(Refer Slide Time: 44:29)

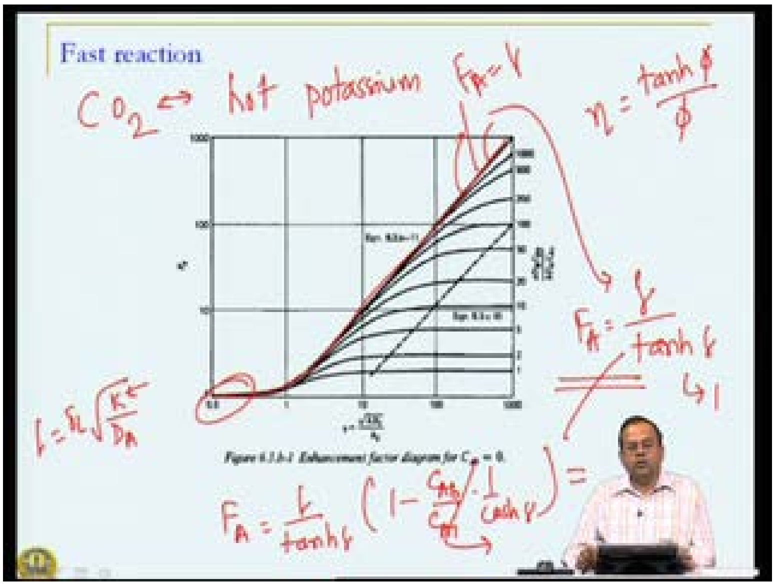


$$\frac{\text{rate of absorption of A observed}}{\text{rate of absorption without reaction}} = \frac{N_A A_v}{K_L (C_{Ai})}$$

$$F_A = \frac{\gamma}{\tanh \gamma}\left(1 - \frac{C_{Ab}}{C_{Ai}} \cdot \frac{1}{\cosh \gamma}\right)$$

So, what would be this would be same as before. But what would have been the rate of absorption. The rate of absorption maximum would have been, see in general it is C A i minus c a b, but let us look at the maximum rate. Let us not worry about this C A b. So, K L into C A i and if you put this two things together, we get and immediately we see that this factor is greater than one. And therefore, this is also referred to as enhancement factor or F A or e. let us look at, if you are not convinced, let us look at actual values and then we will appreciate this.

(Refer Slide Time: 45:33)



Fast reaction

Let’s do not worry about all the other terms, we will come to that. So, what we are seeing here is this enhancement factor which we had written, if A as gamma by tan gamma 1 minus C A b by C A i 1 over cos gamma. So, we are looking at enhancement factor, assuming that bulk concentration of A is very small, depending on the reaction. So, this term goes down or in other words this is nothing but gamma by tan gamma, which is F A. Just to remind you, when we talked about gas solid catalytic reaction our equivalent effectiveness factor was actually tan phi by phi, this is gamma by tan gamma.

If effectiveness factor represented, how would, what is the detrimental effect of mass transfer on reaction. The enhancement factor represents what is a positive influence of reaction to the absorption of the gas. That is how much higher is the absorption of gas with reaction as compared to without reaction and hence the term enhancement factor. And this is what represents that enhancement factor and not surprising to see. This is that behavior that it is close to unity, when gamma value is small. That is gamma small means what? What is our gamma? Our gamma as we defined earlier is a measure of reaction rate by diffusivity into delta l and so on.

So, if gamma value is very small that would imply that reaction rate constant is very small. Whether you have a reaction or no do not have a reaction the rates are pretty much same that is when F A is equal to unity. But if reaction rate constants goes on increasing, as we saw for some of the reactions. We noticed that the value of effectiveness factor or enhancement factor in this particular case. now because tan gamma goes to one as gamma is large. So, this is essentially F A equal to gamma.

If gamma value is thousand, we would have thousand times more absorption of gas as in the liquid as compared to the case, when gas was not reacting with the liquid. This now explains why carbon dioxide for example, is absorbed in hot potassium or alkali solution. Why? you can try to absorb gas carbon dioxide in water at ambient condition, but very little will be absorbed. So, would not be an efficient C O 2 removal scheme. But with potassium hydroxide, it will react and because of that reaction you will have higher absorption of or removal of C O 2.

Another aspect, why hot? Because reaction rates are higher as temperature goes up. And therefore, provided solubility has not adversely affected or even if solubility is adversely affected, it is now the reaction which is dominantly playing a role. So, you use hot solutions, because temperature higher means higher reaction rates that means, even higher enhancement factors. So, this absorption processes or therefore, combined with chemical reaction, so that you get the enhancement of reaction. So with this, we will close the session for today.

And in this session, essentially we started discussion on gas liquid reactions. Noting that, there are two different types of application areas. One is the purification processes, where you want to remove the gas, it is an unwanted material. So, you want to purify the gaseous stream by getting rid of undesirable elements such as carbon dioxide or sculpture dioxide or H 2 S and so on. And second kind of processes where you actually want to make some desirable product like adipic acid or various different acids, which is done by air oxidation, basically air oxidation processes or chlorination processes. Where you want to actually produce product of interest and that is where gas liquid reactions take place.

The broad framework which is often used for gas liquid reaction is a film theory approach. Where you assume that there is a bulk gas, there is a bulk liquid and there is an interface between these gas and liquid. Each of these phases of gas and liquid are further divided in into two components bulk and the boundary layer. Boundary layer is where all the resistance to mass transfer is located. And therefore, we have concentrations of gas and liquid uniform in the bulk, but they are varying in the in the boundaries.

We also saw that the kinetic rate constant for various reaction, class of reactions. Can vary several orders of magnitudes, while diffusion characteristic irrespective of which reaction or what component is there are more or less of the same order of magnitude. That being the case, we have to use different approaches depending upon how fast or slow are this reaction. Of these, we saw two approaches two different cases today. A case of very slow reaction such that there is hardly any reaction in the boundary, all the reaction whatever can take place can take place only in the bulk liquid. And second case, where there is a moderate rate of reaction, where reaction can take place both in the boundary as well as in the bulk. In the next session, we will look at even faster reactions and wrap up the discussion on gas liquid reactions. thank you