Advanced Chemical Thermodynamics & Kinetics
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Lecture - 32
Introduction to solution phase reactions dynamics 02

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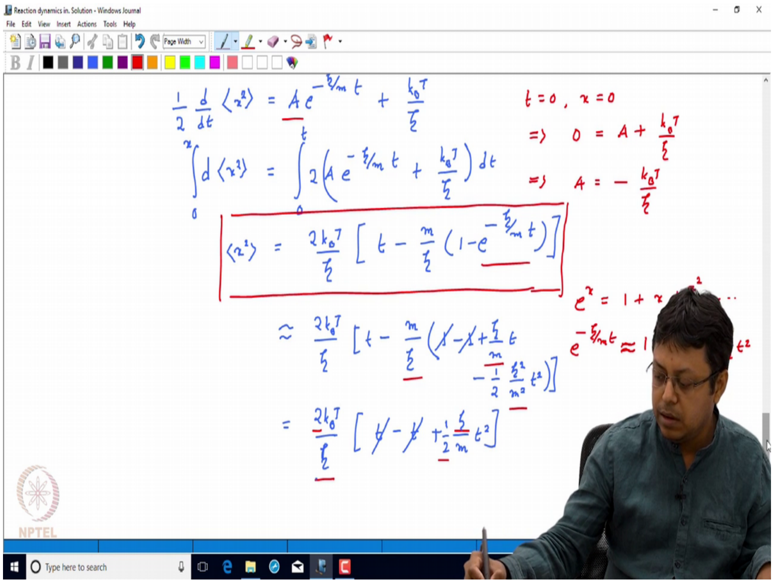

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = \underline{A}e^{-\zeta/m\,t} + \frac{k_BT}{\zeta}$$

$$\int_0^x d\langle x^2\rangle = \int_0^t 2\left(Ae^{-\zeta/m\,t} + \frac{k_BT}{\zeta}\right)dt$$

$$\boxed{\langle x^2\rangle = \frac{2k_BT}{\zeta}\left[t - \frac{m}{\zeta}\left(1-\underline{e^{-\zeta/m\,t}}\right)\right]}$$

$$\approx \frac{2k_BT}{\zeta}\left[t - \frac{m}{\underline{\zeta}}\left(\cancel{1}-\cancel{1}+\frac{\zeta}{\underline{m}}t - \frac{1}{2}\frac{\zeta^2}{\underline{m^2}}t^2\right)\right]$$

$$= \frac{2k_BT}{\underline{\zeta}}\left[\cancel{t}-\cancel{t}+\frac{1}{2}\frac{\zeta}{m}t^2\right]$$

$t = 0,\ x = 0$

$\Rightarrow\ 0 = A + \frac{k_BT}{\zeta}$

$\Rightarrow\ A = -\frac{k_BT}{\zeta}$

$e^x = 1 + x \cdots$

$e^{-\zeta/m\,t} \approx 1 \quad t^2$

Now, this equation can be directly integrated. So, it is d of x square average is 2 times A times we can actually write it like e to the power of minus zeta by m into t plus kB T by zeta dt. So, we integrate this one now before integration we could also figure out that what is the value of this constant which is A this constant.

And that we can set very easily like we know that the from initial condition that at t equal to 0 we can take x equal to 0. So, that will give us the left hand side will be 0 and then that is equal to A times e to the power minus 0 is 1 plus k BT by zeta. So, that will give us A is minus of k BT by zeta, so that we can easily incorporate here and then do the integration.

So, the limits are again at t equal to 0 x is equal to 0 at t is any arbitrary time. So, the position is x and then we will get after we put the value of A we get x square average is equal to twice kBT by zeta. So, you can actually check this integration times t minus m by zeta times 1 minus e to the power minus zeta by m into t.

So, this gives the mean square displacement I mean this is the full analytical solution. But we can know approximate because as you can see here I have a exponential term and you know that e to the power x is nothing, but 1 plus x plus x squared by 2 factorial which is 2. And this way you can actually write the series and we can truncate it up to certain terms because we can see here that it is basically zeta divided by m, now m is the mass of the particle if the mass of the particle is large.

So, then actually you can make this approximation and we can ignore the higher order terms. So, if we do that what we will get is twice kBT by zeta and t minus m by zeta and then within parentheses you have 1 minus so e to the power of minus zeta by m times t will be. So, x is basically minus zeta m by t 1 minus zeta by m into t plus zeta square divided by m square into t square and there is a 1 by 2.

So, up to that point we are truncating the series, so we can actually put the values here and we can see this one actually will get cancelled very easily. And then this minus sign becomes plus here plus zeta by m into t and then this plus sign becomes minus here it will be minus half zeta square by m square into t squared .

So, we can actually apply I mean again arrange it twice kBT by zeta and this 1 gets cancelled. Now I am actually multiplying by m by zeta, so this actually cancels with this zeta by m. So, what I will be having is the first term is t minus t so that t also gets canceled and then what we will have is we will have a plus sign here and the m by zeta actually gets cancelled with one zeta by m zeta by m squared.

So, I will be left with one zeta by m times t squared, so this t will again get cancelled. So, what ultimately we will get is we have another zeta will get cancelled with this zeta as you can see this one and this one get cancelled. So, what ultimately will get is and also there was a two factor I forgot to include that, so there was a half factor and then this two also gets cancelled these two gets cancelled with this. So, ultimately we will get an expression for the mean square displacement as this just write it in the next page.

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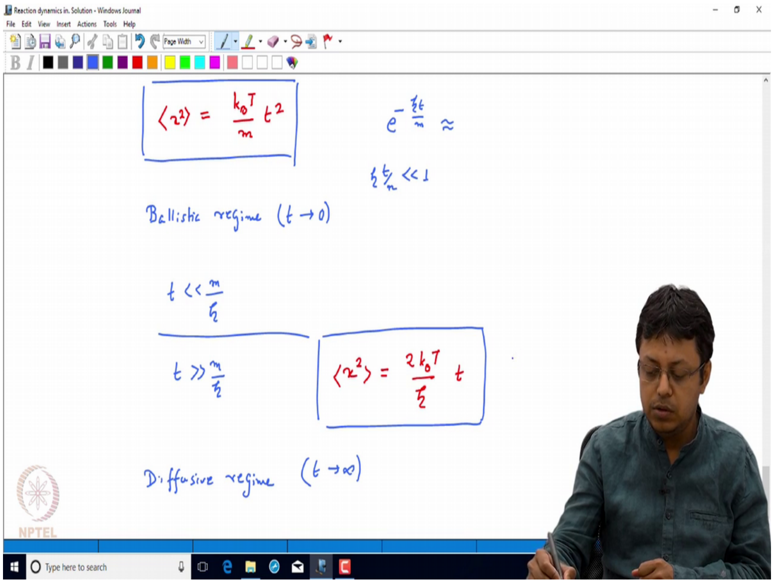

$$\boxed{\langle x^2\rangle = \frac{k_BT}{m}t^2}$$

$$e^{-\frac{\zeta t}{m}} \approx$$

$$\frac{\zeta t}{m} << 1$$

Ballistic regime $(t \to 0)$

$$t << \frac{m}{\zeta}$$

$$t >> \frac{m}{\zeta}$$

$$\boxed{\langle x^2\rangle = \frac{2k_BT}{\zeta}t}$$

Diffusive regime $(t \to \infty)$

So, what we will get is x square average is kBT by m into t square. Now what we have done here is basically known as the ballistic regime in the sense that if the in this formula as you can see if what we have made an approximation that in the very small time scale this will be correct. In the sense that if you remember that we when you made this approximation we wrote that these e to the power minus zeta t by m that ultimately we took the three terms right.

And these three terms means actually this t by m is much less than 1 when m is large or time is very small, so in that limit when t is going to 0. So, we have actually the mean square displacement going as t squared, so this regime is known as a ballistic regime when actually t goes to 0. Now if we think about the other limit in the sense that t is very large then actually we will what will see here that this value the kBT by m to the power of half.

So, we can actually write it in this way, so you can go back and look at your exponential. So, if the time is very large so or t is much smaller than m by zeta. So, this is this actually corresponds to the ballistic motion as we have seen here. So, it will be zeta t by m that much greater less than 1 or t by t is much smaller than m by zeta, so when time actually goes to 0 I mean very short timescale. Now in the other time limit when actually t is much higher than m by zeta. So, then we can actually assume that in the in this equation that x square average you can easily figure out what the result will be you can easily figure out from this equation where I have x square is equal to the original equation that is twice kBT this equation where we had a full analytical equation.

And if we do not make that approximation, then actually you can keep that and then you can show that and this time regime it will be nothing, but twice cavity. So, because the zeta will cancel out it will be something like twice kBT by zeta into t. Now this regime when is valid when actually t goes to infinity or in the long time limit and this is known as the diffusive limit or in the Brownian limit, so it is in the diffusive regime. Now, this mean square displacement equation again you can actually figure it out and we will we will show you in a handout how basically it comes.

So, do not make this approximation that do not truncate these series up to this point and then you can actually ignore. So, the entire term e to the power minus zeta by m into t because that that is a very small number now and then because actually your it us basically goes as e to the power minus infinity and because t is very large and then one what you can do is that you can just keep the first term which is one.

So, it will be just t minus m by zeta, but again t is very large so all you will be left with is this term which is just t. So, that is how it this equation you get, now this was shown by Einstein, but he also predicted that at a very short time you will have a balance sheet regime where actually the mean square displacement will go as t squared. And at a very longer time you will have a diffusive regime where actually means square displacement will go with time.

Now, we can actually go back and use the mean square displacement formula that we just developed. In the sense that if you remember that we were talking about diffusion and there we solved the rms deviation so, we are using a z notation in this case I will use x notation because x and z are just arbitrary.

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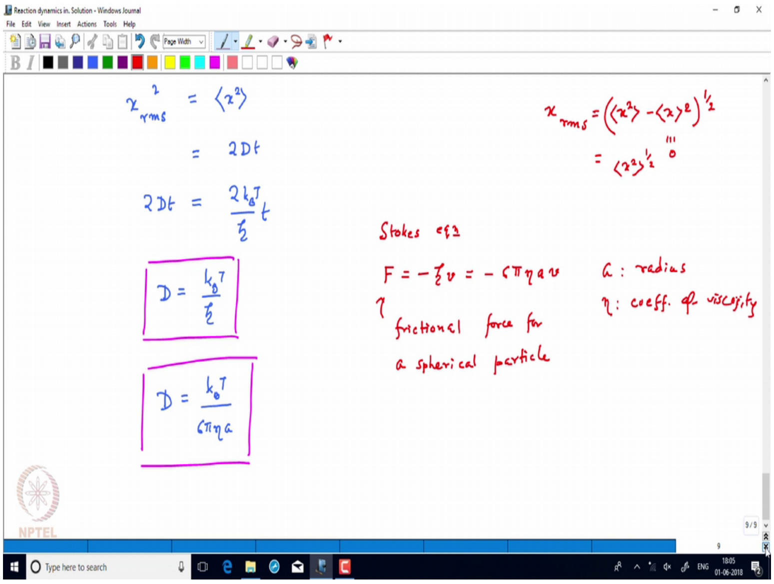

$$x_{rms}^2 = \langle x^2 \rangle$$
$$= 2Dt$$
$$2Dt = \frac{2k_BT}{\zeta}t$$
$$\boxed{D = \frac{k_BT}{\zeta}}$$
$$\boxed{D = \frac{k_BT}{6\pi\eta a}}$$

$$x_{rms} = \left(\langle x^2 \rangle - \langle x \rangle^2\right)^{1/2}$$
$$= \langle x^2 \rangle^{1/2}$$

Stokes eqn

$$F = -\zeta v = -6\pi\eta a v$$

frictional force for a spherical particle

a : radius

η : coeff. of viscosity

So, this rms deviation or the root mean square deviation x rms square of that is nothing, but x square average in this case x rms is a x square average minus x average squared and the square root of the entire thing. But, it is basically root mean square deviation, but in this case the x average we are taking it to be 0.

So, that is why it is nothing but the x square average and square root of that so that is why I am writing it directly as x square average. And that we already know from the diffusion equation which we already saw a little bit earlier it is it goes as twice Dt to the power half, now what we got just now in the diffusive regime x squared average is twice kBT by zeta into t. So, you can actually equate these two equations and we will get that this is if I take the squared of this quantity.

So, it will be just there will be no half because; this half is only for the rms thing and we were taking the rms squared. So, what we see here that twice kBT or twice Dt is nothing, but twice kBT by zeta into t and now you can get a very handy expression for the diffusion coefficient which is kBT by zeta.

Now you can actually further use the expression for zeta is again a frictional coefficient. Now you can use actually a stokes formulation where he said for a spherical particle this zeta or the or basically the force which acting acts on a Brownian particle or a spherical Brownian particle will be nothing, but minus zeta into it is the velocity. Because we have to use this force if you remember that we wrote that m into acceleration mass times acceleration is this opposing force which is the frictional force.

And frictional force for a spherical particle will be nothing, but minus 6 phi eta a into v, but this a is the radius of the particle and eta is the coefficient of viscosity coefficient of viscosity. Now we can see that the diffusion coefficient now we can connect it to the coefficient of viscosity and that is a very interesting equation that we can write that it is kBT by zeta and in place of zeta we can write 6 phi eta into a. So, this is from stokes equation and this force is nothing, but the frictional force for a spherical particle.

Now, we can move on and we can actually use this concept of diffusion which we just I have developed to understand what will be the a general formulation of any reaction in solution. Because, ultimately we want to express the rate constant in a solution which are actually diffusion limited. In the sense that the rate determining step is basically the overall rate is basically determined by how these two species or two reactants are encountering each other. And we are saying that can assume that every encounter can lead to reaction which means that reaction is not limited by the encounters because, whenever they approach each other they will definitely encounter and every react encounter will give reaction.

However, now we are limited by how many encounters are happening because these two reactants are just like two partners and they have to define the partner in solution because they are moving now in a crowded environment and they are basically diffusing; now we can actually develop a model based on that.

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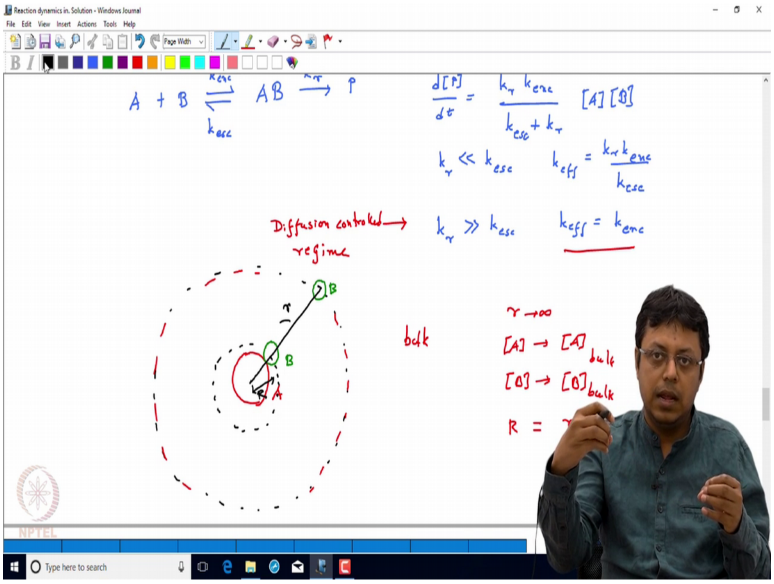

$$A + B \underset{k_{esc}}{\overset{k_{enc}}{\rightleftharpoons}} AB \xrightarrow{k_r} P$$

$$\frac{d[P]}{dt} = \frac{k_r k_{enc}}{k_{esc} + k_r}[A][B]$$

$k_r \ll k_{esc}$ $\quad k_{eff} = \frac{k_r k_{enc}}{k_{esc}}$

Diffusion controlled regime → $k_r \gg k_{esc}$ $\quad \underline{k_{eff} = k_{enc}}$

$r \to \infty$

$[A] \to [A]_{bulk}$

$[B] \to [B]_{bulk}$

$R = r$

So, the language which I just told is something like already known to you I have two reactant say and then we are forming some complex which I already wrote many times and then we have some forward rate so we call it as a encounter rate. And then there is an escape rate and then this A B in the second step actually forms a product and this is basically the rate of the reaction or rate of product formation. Now we know actually under steady state approximation we can write the rate of product formation we have done it many times and that is nothing, but k the reactive rate constant times the encounter rate constant divided by the escape rate plus the reactive rate times A times B.

So, this is just by molecular reaction in solution it is the same formula which we use for gas phase reaction. Now and again if you remember that if we think that this k r is much smaller than the ks cap which means the reaction is basically limited by the reactive rate then actually overall it is a by molecular reaction. So, I will have the effective rate constant as something like k r k s cap divide sorry k encounter divided by k s cap.

So, which means actually the rate is limited by the last step so the encounters are basically small. But, we are not considering that limit we are considering the other limit where the reactive rate is much faster than this escape rate which means the effective rate is nothing, but as you can see if I keep the k r in the denominator. And ignore the k s cap then actually the k r gets cancelled with k r in the numerator and all I will have the reaction rate is dependent on the encounter rate. So, I this regime is basically the diffusion controlled regime because, it is the encounter rate that matters so, it is the diffusion controlled regime,

So, we are going to actually formulate that now. Now the question is how will you formulate it? Suppose we have two reactants A and B and what we are going to ask is that fine. So, the then there will be a flux of A molecules into B and then there will be a similar flux of B molecules into A. So, overall the way it will look like is something like this I have a say a molecule of A.

And then suppose I am writing the B molecule in a different color suppose this is the B molecule. So, there is a radius within which a sphere within which the A and B the B should be there otherwise the reaction will not occur. So, this basically the we are again considering this as a hard sphere model just like we did, but the question here is that this B is coming from a distance which is let us say at a distance r. And then what we can think that there is a bigger radius from where this B is coming from.

But, so all we have to do is basically calculate what is the flux of these B molecules towards A or equivalently what is the flux of A molecule towards B? So, if you can calculate that then we are done because that will be connected to my rate constant because, now it is limited by the diffusion as we have seen it. So, encounter is nothing, but basically how they are finding the partners each other. Now the interesting question which you can ask here is this that fine I have A molecule would B and B is coming, but then what is the symmetry of the problem. In the sense that it is not like happening in the two dimensional plane as I have drawn here.

So, there is a B molecule like let us say there is A molecule at the center the way I have drawn it. Now the B can approach an any direction in regardless of the angle of approach, which means actually we can actually think the entire problem in a spherical polar coordinate that is number 1.

And number 2 is that as the B and A encounter and we are assuming that k reaction is pretty fast meaning that the every encounter is giving a reaction which means actually there will be a depletion of B molecules and the A molecule which will create a concentration gradient. Similarly, in this picture actually it is a it is in a relative frame where actually A is static and B is moving, but you can think in the other way that A r also relatively moving to the B.

And then which means actually the concentration of A around B will also deplete which will create a concentration gradient for A also, but it is the same reaction because the A and B are I mean k r basically encountering and the product is being formed and as a result both concentration of A and B are depleting. So, since it is the same mechanism the gradient for A and B also you can assume to be identical. Now, in order to approach this problem let us first start with our the formula for reactive flux in this case we will just use the flux and we connect it to the reactive flux later.

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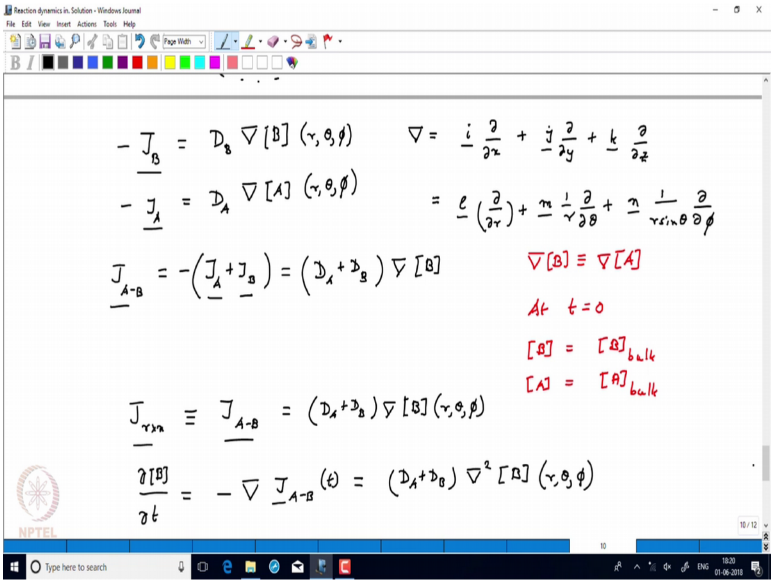

$$-\underline{J}_B = D_B \nabla [B] (r,\theta,\phi) \qquad \nabla = \underline{i}\frac{\partial}{\partial x} + \underline{j}\frac{\partial}{\partial y} + \underline{k}\frac{\partial}{\partial z}$$

$$-\underline{J}_A = D_A \nabla [A] (r,\theta,\phi) \qquad = \underline{l}\left(\frac{\partial}{\partial r}\right) + \underline{m}\frac{1}{r}\frac{\partial}{\partial \theta} + \underline{n}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

$$\underline{J}_{A-B} = -(\underline{J}_A + \underline{J}_B) = (D_A + D_B)\nabla [B]$$

$$\nabla [B] \equiv \nabla [A]$$

At $t = 0$

$$[B] = [B]_{bulk}$$

$$[A] = [A]_{bulk}$$

$$\underline{J}_{rxn} \equiv \underline{J}_{A-B} = (D_A + D_B)\nabla [B](r,\theta,\phi)$$

$$\frac{\partial [B]}{\partial t} = -\nabla \underline{J}_{A-B}(t) = (D_A + D_B)\nabla^2 [B](r,\theta,\phi)$$

So, the flux as we know is let us say flux of B molecule that we are writing as minus J B because there is a in the flux efficient there is a minus sign, I am writing the minus with the flux equation and that is basically diffusion coefficient of B times. Now, these flux I am considering round in three dimension, so this is a vector quantity I should use a underscore or a boldface J of B.

So, I am just using a underscore for vector and this is the diffusion coefficient and then I have a three dimensional gradient of concentration of B and which this concentration is now dependent on r theta and phi. And similarly, I can also write it for A the flux which is a vector quantity again is nothing, but the diffusion coefficient of A and the gradient of A as a function of r theta and phi.

Now, what is this gradient now this gradient again is a vector quantity which is i del del x plus j del del y plus k del del z which is written in a Cartesian coordinate rectangular

Cartesian coordinate where ijk and the unit vectors along x y and z direction. But we are more interested in solving this problem in spherical polar coordinate and in there the del takes the form like the unit vectors if I write it as A B and or A suffix phi or we can write it any you can choose any I mean notation.

Let us say we let us do it as lets l m and n. So, l is basically the unit vector along r, so it will be a del del r plus m is the unit vector along theta. So, it will be 1 by r del del theta and n is the unit vector along phi which will be 1 by r sine theta del del phi. Now this transformation probably you have seen you can you have to write x y z in terms of r theta phi or r theta phi in terms of xyz and then take the partial derivatives.

And then you can actually get this gradient in the spherical polar coordinate this you have probably seen when you did some problem in spherical polar coordinate for example, the hydrogen atom problem ah. So, there actually use this there actually use the del square also which we also need subsequently.

Now, what I am saying here is that now J I have a flux of A molecules towards B and B molecules towards A. So, the net flux will be basically the addition of the two flats and this net flux I am keeping to be calm to be basically A positive. So, that I define the net plus not as JA plus JB, but actually negative of J plus J B. So, that I keep the net flux notation to be positive, so it will be very straightforward it will be basically DA plus DB times the gradient of B.

Now, in this case again remember that I have assumed that the gradient of B is basically identical to the gradient of A. Because, the gradient is being created by the same mechanism when A and B are encountering both vanish and the p emerges and that is why the gradient is formed. And so the A and B gradient should be basically equal that is an approximation, but it is a very valid approximation under this model.

Now, what we can say here is that so, the A and B are basically coming and there is a suppose at time 0 basically the reaction starts and A and B are approaching each other. And then once they encounter there is a concentration gradient which sets in and then again more and more nb actually approach with to each other and there will be a reaction and sooner or later there will be a steady state which will be reached. Now, before we started at t equal to 0 everything had a bulk concentration meaning the B at t equal to 0.

So, we can approximate at t equal to 0, the B is basically equal to B of bulk we are just writing it as a A high suffix at as bulk and similarly A was also A of bulk. So, these are the basically bulk concentration and these bulk concentration is do not change over time because, this is just A bulk concentration and then over time what is happening there is a local concentration changing. So, we are we are assuming that there is a reactive sphere something like we have drawn here.

So, this is the reactive sphere and this reactive sphere outside this reactive sphere there is basically there is bulk. So, when this r or the radius of the encounter or the distance between these two pairs reactant pairs is very large when r tends to infinity this A will tends to A bulk and B will also tend to B bulk. And A and B bulk are not influenced by the reaction which both of them are basically independent of time that is an assumption we are using. Now we can actually use the flicks second law in the three dimension because, we actually showed it for one dimension case, but it is the same thing.

And then basically we are saying that since all the encounters are giving me reaction the reaction encountered is nothing, but identical to the diffusive encounters itself. And for which we have a formula which is DA plus DB into gradient of either A or B we are writing it in terms of B and they can B is dependent on r theta and phi. Now we can actually say that what is the time derivative of this concentration, what is DB DT? Again B is basically the local concentration not the bulk.

Whenever, we are using the bulk concentration we will write suffix bulk so DB t. So, that we know that we are basically extending the one dimension to three dimensional problem that is basically the gradient of the flux itself the joint flask which is a time dependent quantity. And that is nothing, but DA plus DB now J itself as you can see in the earlier expression that it is a gradient of B. So, it will be now actually del square of B of r theta and phi. Now the question is what is the form of del square in like we have already talked about the form of a del.

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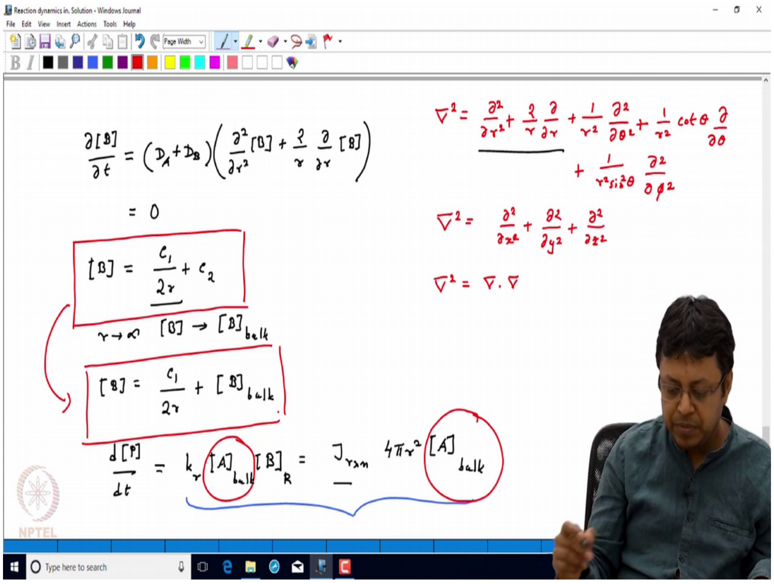

$$\frac{\partial [B]}{\partial t} = (D_A + D_B)\left(\frac{\partial^2}{\partial r^2}[B] + \frac{2}{r}\frac{\partial}{\partial r}[B]\right)$$

$$= 0$$

$$\boxed{[B] = \frac{c_1}{2r} + c_2}$$

$r \to \infty \quad [B] \to [B]_{bulk}$

$$\boxed{[B] = \frac{c_1}{2r} + [B]_{bulk}}$$

$$\frac{d[P]}{dt} = \underbrace{k_r [A]_{bulk} [B]_R = J_{rxn} 4\pi r^2 [A]_{bulk}}$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2 = \nabla . \nabla$$

Now, in spherical polar coordinate the del square is can be written as del 2 del r 2 plus 2 by r del del r plus 1 by r square del 2 del theta 2 plus 1 by r square cot theta del del theta plus will have 1 by r square sine square theta del 2 del phi 2. So, this is the overall these spherical polar one and the Cartesian one is very straightforward it will be if I write the del square. So, it will be just del 2 del x 2 plus del 2 del y 2 plus del 2 del z 2.

Now see here the del is an vector quantity because, it is it depends on i three vectors i j and k unit vectors. But, del square is a scalar quantity because del square is nothing, but del dot del and if I consider del to be a vector this del square is a scalar because this is a dot product. Now we can actually think that all this B or the concentration variation is actually varying radially independent of the direction.

So, all we have to consider here so that del del theta del del phi or those are basically 0, which means there is no angular variation as we said at the beginning and all the variation is basically the radial variation. So, we can write away instead of writing the del square in the full form we can just write the only the radial coordinate variation, so let us just write it.

So, dell B del t will be DA plus DB times I have del square of B. So, you see here that del square I will just consider these first two terms so it is del del 2 del r 2 of B plus 2 by r del r of B. So, when the steady state is reached this should be 0, when we have reached an equilibrium that the reactions forward and reverse if turn happening at the same rate and you have a steady rate of product formation. So, under the steady state because it is all under steady state approximation we can think that the time derivative of the B is basically 0.

Which means actually if what the way we should think about it now is that there is a bulk concentration which is very high and then there is a reactive zone and within the reactive zone actually the reactants are continuously being flown. Now, which means actually of course, the reactants are being depleted in the bulk due to diffusion, but we are assuming that the A bulk and B bulk does not change because, the concentration is too high. But only in the near the vicinity of A the B is changing and similarly the under facility of A also is in vicinity of B also A is changing.

Now, we can actually right away solve this equation and the solution will be B is nothing, but and again and this B is a function of the radial coordinate B is C 1 by 2 r plus C 2, where actually C 1 and C 2 we have to determine. Now we can use the boundary condition like we already know that r tends to infinity A tends to or B tends to basically B equilibrium. So, we can right away see that if r tends to infinity this term will be 0, so C 2 is nothing, but B equilibrium so, B is sorry not B equilibrium it is basically B bulk .

So, we can right away rewrite that B is C 1 by 2 r plus B bulk. Now what is the rate of product formation that is what we are interested in and we already wrote that the rate of product formation dP dt. That is basically equivalent to the reactive rate constant times the concentration of A in bulk because, we are thinking that actually B is coming and B is basically depleting.

And so the local the way I have drawn it basically d is B is vanishing. So, the a concentration we are saying that it is not changing because at you can think it like this that there is a bulk A concentration and then only the B is approaching, because it is all relative motion. So, therefore, B actually we have to consider the local concentration of B and that we already know that this is nothing, but if I just integrate the B equation. Now, you know that what is the B equation, B equation is nothing, but it should be the rate should be the flux which is the reactive flux which we already have talked about.

And then I will have a basic idea of volume within which this flux is happening. So, fluxes again basically they a flow per unit area per unit time and then I have to also consider the volume currently the volume I am considering the reactive volume or the reactive zone is basically a sphere with a radius smaller.

So, the overall volume will be 4 phi r square. So, this is basically the number of how many A molecules are there the or how many sorry how many B molecules are coming that we are calculating. So, is nothing, but now multiplied by 4 phi A squared that is the following times the A bulk A bulk we are not touching. Now, we can write the expression for the reactive flux which we have already got here J reaction. So, what we can write is proceeding from this relation.

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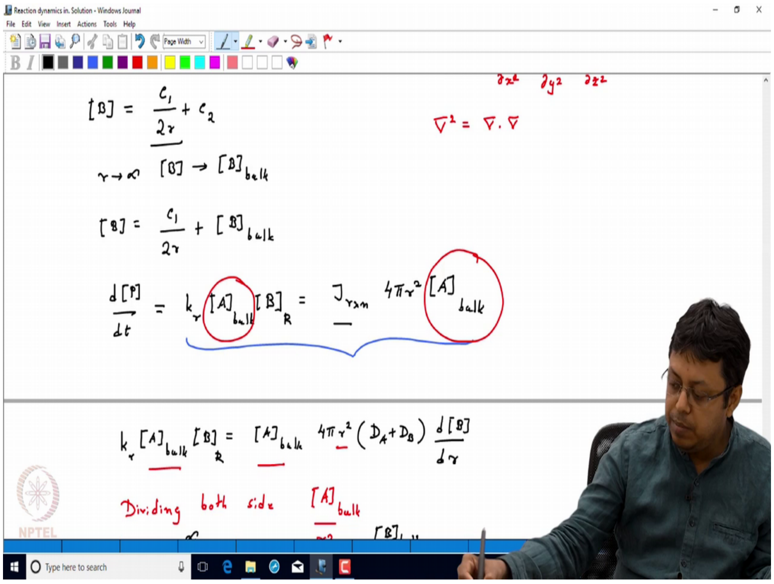

$\partial x^2 \quad \partial y^2 \quad \partial z^2$

$$[B] = \frac{c_1}{2r} + c_2$$

$$\nabla^2 = \nabla \cdot \nabla$$

$$r \to \infty \quad [B] \to [B]_{bulk}$$

$$[B] = \frac{c_1}{2r} + [B]_{bulk}$$

$$\frac{d[P]}{dt} = \underbrace{k_r [A]_{bulk} [B]_R = J_{rxn} 4\pi r^2 [A]_{bulk}}$$

$$k_r [A]_{bulk} [B]_R = [A]_{bulk} 4\pi r^2 (D_A + D_B) \frac{d[B]}{dr}$$

Dividing both side $[A]_{bulk}$

So, in the next step we are writing as k r which is the reactive rate at a basically it is a final step rate times the a bulk actually is on both side. But we are just keeping it first I mean we will see what it will have A bulk times B that is basically equal to A bulk times 4 phi r squared. And instead of flux right we are now using DA plus D B the reactive flux is exactly equivalent to the overall flux and then I have the time derivative of B and which we just solved.

So, this is coming from the flicks second law of diffusion and now the interesting thing is that now you can actually write down the equation for the B bulk. So, we can actually divide both side by A into r square. So, let us just write it dividing both side we could have removed the A bulk about I in the beginning because you can see that it is a common term. So, dividing both side A bulk and then I will also divide it by r square.

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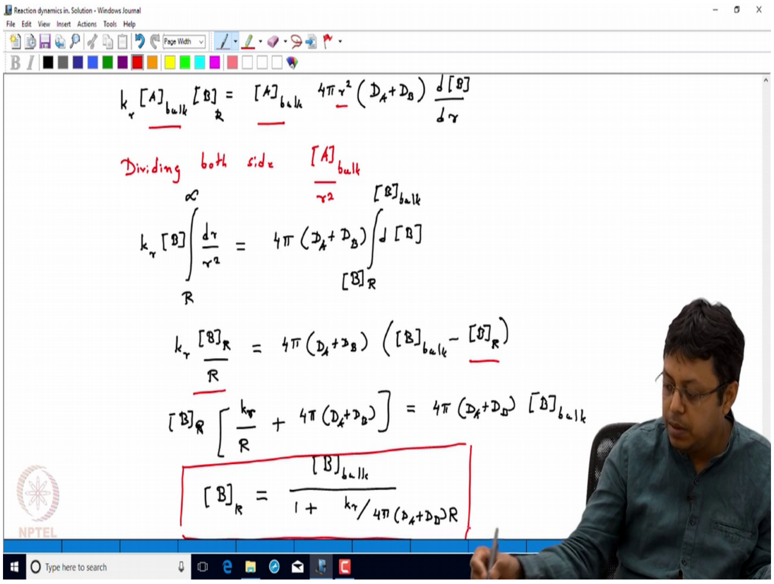

$$k_r \underline{[A]_{bulk}} [B]_R = \underline{[A]_{bulk}}\, 4\pi \underline{r^2} (D_A + D_B) \frac{d[B]}{dr}$$

Dividing both side $\frac{[A]_{bulk}}{r^2}$

$$k_r [B] \int_R^{\infty} \frac{dr}{r^2} = 4\pi (D_A + D_B) \int_{[B]_R}^{[B]_{bulk}} d[B]$$

$$k_r \underline{\frac{[B]_R}{R}} = 4\pi (D_A + D_B) \left([B]_{bulk} - \underline{[B]_R}\right)$$

$$[B]_R \left[\frac{k_r}{R} + 4\pi (D_A + D_B)\right] = 4\pi (D_A + D_B) [B]_{bulk}$$

$$\boxed{[B]_R = \frac{[B]_{bulk}}{1 + k_r / 4\pi (D_A + D_B) R}}$$

So, what you will get is a little bit compact form which is k r I have the B B is the local concentration again and then what I have is I have dB r. So, this is this should not be the time derivative this should be the space derivative because is just the equation for the flux as you can see here. So, these flux is basically the how things are approaching with each other and that is basically the concentration gradient dependent on the concentration gradient and since this is only radially fading. So, this is just a del del r of B, but we are not using the dell notation right now because it is independent of theta and phi.

So, we can actually write it as dd r because the only variable is a special variable is r. So, we can actually write it as d r by r square is basically equal to 4 phi r square already we have removed DA plus D B into dB. What we are going to do is basically now of course, we are going to integrate this equation and remembering the fact that if I integrate it at say at a particular distance which is let us say at a distance let us say r which is a which actually is this distance. Because, this distance is important because all I have to calculate is what is the basically local concentration and flux at that point because at that point these two species are basically touching each other.

So, capital R is basically the radius or the capital R is basically the radius of A plus radius of B. So, that we have already discussed in many situations like when we talked about the excluded volume in minerals equation or say when you talk about the reaction in gas phase or basically, we derived the mean free path or collision in gas phase we always talk about the cross section.

And this cross section is nothing, but in a linear case so that the molecule will feel a cross section and we say that it is basically the cross section I can actually write it as an area circular area. But, the radius is basically the addition of the radius of the two species and it makes sense because if we just make that condition to happen then the collision will happen. But, if the distance is more than this critical distance these hard spheres should not touch each other and there will be no collision.

So, the lower limit is R here and so basically it is a the in this case the lower limit is B at R and which happens at a location R. And at infinity this distance or infinite distance this B will be nothing, but equivalent to B bulk, which you already are good. Now, if we do this integration so, it will be nothing, but it is a very straightforward integration. So, what we will have is k r now the B at a distance R divided by R.

So, I am writing actually the one, so this 1 by R actually it comes from the integration of 1 over R square. And then I have on my right hand side DA plus DB and then it is just an integration of B ok. So, when I write this thing since we are writing the local concentration as B R let us also use this notation here it should be B R because, if you remember the what is happening here I have a bulk concentration of A.

So, A is everywhere and I am fixing the A as if A is not moving and B is are moving a B is coming and B is actually is touching the DA and at that location I am calculating the flux of B. And then B is vanishing and there is a concentration gradient that we are we have already worked out. But, the interesting thing is that when B is coming and it is basically touching we have to actually concentrate at that location otherwise the encounter will not happen. So, what we are doing here is 4 phi DA plus DB and then we have this right hand side integration is very straightforward it is basically B at R equal to infinity minus B at R equal to R.

So, that already we told that this is basically B bulk minus B R. So, now this B R thing we can take common and we can write as B R into k r k suffix R this is a reactive rate. We could have written it as a k 2 just to distinguish between small r and this reactive r and then I had there is a minus sign. So, it will be plus sign if we just bringing this term on the left and adding with this term. So, there is a constant which is 4 phi DA plus DB and that on the right hand side we have 4 phi DA plus DB times B bulk.

So, you can now easily solve it so, this is B R what is the value of B R. So, this is basically the concentration of B in the vicinity of A and that is nothing, but equal to the B bulk its bulk concentration divided by this entire thing which is if I just rearrange it is a little bit, because I see that there is a 4 phi DA plus DB. So, I can divide the numerator and denominator by 4 phi DA plus DB it will be 1 plus k r divided by 4 phi DA plus DB into R. So, this is the overall expression for B in the vicinity of the concentration of B in the vicinity of A.

So, that we are now going to use now already if you remember that we that why we need that because remember that we calculated the concentration of B the time dependence. And then it basically reduced to a another equation after we wrote the bulk form that B at any position any position you can write it as C 1 by 2 r and plus B of bulk. So, that we are now going to use that what is basically the B because, we need the values of c 1 and c 2 also now c 1 you can easily calculate.

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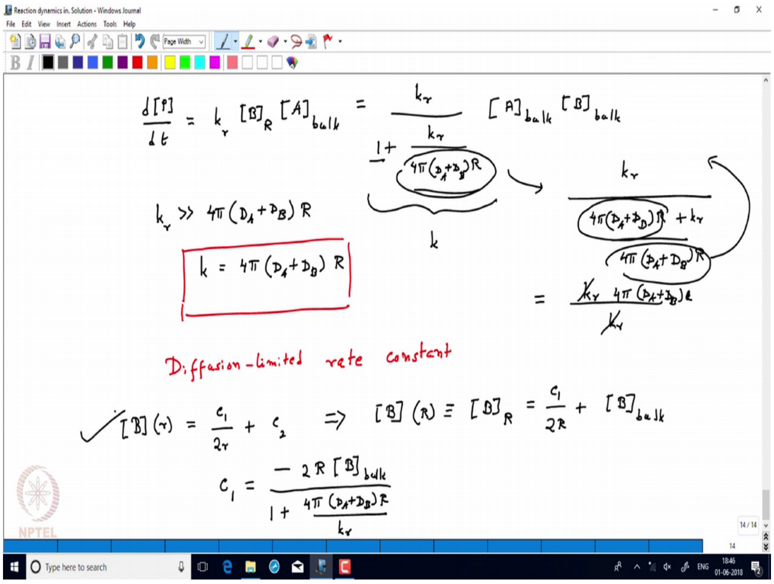

$$\frac{d[P]}{dt} = k_r [B]_R [A]_{bulk} = \frac{k_r}{\underbrace{1+\frac{k_r}{4\pi(D_A+D_B)R}}_{k}} [A]_{bulk} [B]_{bulk}$$

$$\rightarrow \frac{k_r}{\frac{4\pi(D_A+D_B)R + k_r}{4\pi(D_A+D_B)R}} = \frac{\cancel{k_r}\, 4\pi(D_A+D_B)R}{\cancel{k_r}}$$

$$k_r \gg 4\pi(D_A+D_B)R$$

$$\boxed{k = 4\pi(D_A+D_B)R}$$

Diffusion-limited rate constant

$$✓\ [B](r) = \frac{c_1}{2r} + c_2 \Rightarrow [B](R) \equiv [B]_R = \frac{c_1}{2R} + [B]_{bulk}$$

$$c_1 = \frac{-2R[B]_{bulk}}{1+\frac{4\pi(D_A+D_B)R}{k_r}}$$

Now, this is not necessary because all we are interested is basically to calculate what is the rate of product formation? And remember that is nothing, but A bulk, so let us write it once again. So, it is in the reactive rate times the local concentration of B times the bulk concentration of A which is nothing, but now we have already solved it the local concentration of B. So, it will be nothing, but k r divided by 1 plus k r by 4 phi DA plus DB into r times A bulk times B bulk.

Now, if the encounter rate is very fast which we actually already made an assumption that this rate is much faster than the diffusion rate and the diffusion rate is given by 4 phi again the 4 phi is coming from the spherical symmetry it is a total solid angle. So, it is DA plus DB at times R, so 4 phi R is basically the volume around A. So, this is the closest approach volume and then if I multiply by the diffusion coefficient, so that if that quantity is much smaller than the reactive rate.

So, we can actually ignore this as you can see here 4 phi this term actually we are writing it to be much smaller than k r. So, then actually we can write the overall rate expression as if I consider this entire term as the k effective or the k of this reaction.

So, we can actually write it as the k is 4 phi DA plus DB into R. Now, how it comes it is very easy because as you can see that this term is in the numerator. So, I will just write it as 4 I and I will write it as 4 phi DA plus DB into R because it is multiplied by 1 plus k r and then I am ignore that term. So, do new my denominator it will have only k r and this let me just show you what I am saying.

So, it will be k r divided by 4 phi DA plus DB into R plus kr divided by 4 phi DA plus DB into R, now this term we can actually ignore with respect to k r. So, that we can write it as k r and this term now go in the numerator into 4 phi DA plus DB times R divided by k r and this k r actually gets cancelled, so that is how we are getting it. So, this is basically the overall rate constant which is the diffusion limited expression for the diffusion limited rate constant and that is what we wanted to calculate.

So, the overall rate or the composite rate of this reaction when the last step is very fast the k r is very fast we see the product basically gets formed with a rate which is equal to 4 pi R where R is capital R it is basically the closest approach distance and times the DA plus DB. So, this is what we wanted to do and to find out an expression for the diffusion limited rate constant. So, this is the diffusion limited rate constant, now we will have complications when these species are ionic species because, whenever they are there charged species so there will be a repulsion and if their opposite charge there will be an attraction.

So, we can actually use the same you know formulation in the sense that A and B are approaching each other and the same diffusion equation, but the only thing we have to plug in very carefully is the repulsion. And that we will see later, but just to give you a feeling that we also were deriving this time derivative because we used flicks second law at some point. And we used basically the time derivative is 0 and then we solved for B for any position that we wrote it as C 1 by 2 r although you we not use it and this just to give you a feeling that how you can actually get the steady state concentration of B.

But, then we only solve basically the value for C 1, but not for C 2 sorry not for C 2 and C 1 was we did not solve. Now the C 1 you can easily figure out because we have already got an expression for B attained at an position R. So, from that actually it can actually work it out on your own, the expression for C 2 that you should get sorry not C 2 it is C 1. The expression for C 2 C 1 that you should get is let me actually rewrite the earlier equation once again. So, we got basically B at any arbitrary location let us say at a location r is nothing, but C 1 by 2 r plus C 2.

So, what we can say is that B at a location R is basically capital R which actually we wrote as B suffix R that should be C 1 by 2 R plus C 2 and C 2 already we figured out it is nothing, but B bulk. And then B R already we solved which is this equation and now you can see that what the way we have to do it is basically I have to add 1 B bulk to it. And then I can easily solve for C 1 and if you do it the expression for C 1 will be minus twice R times B bulk divided by 1 plus 4 phi DA plus DB times R divided by k r although we did not use it.

Thus you can see that I can actually get the value of B which we actually wrote in this equation at any position. And so this is a general equation for the value of the concentration of B at any position with respect to the A. Now here one question that you might think is that why we were using the in this equation when we are actually discussing the rate of the reaction why we were using A as a bulk A bulk because, we said that why it is not a local thing now the concept here is that you can think that ok.

So, there is a bulk concentration of A and B initially at time 0 and suppose there is no reaction we just mixed it there is no reaction at time 0. So, if we can conceptually think about it and at that time every constitution is bulk concentration. Now, the A is sitting at the middle and the B is coming and that is how we actually modeled our system, but we said that the flux actually is in both ways.

So, the reactive flux is actually both j a is contributed by j a and jb, but you can actually cause the entire problem in the as if the A is static and B is moving. This is the same thing you do when two particles come closer together and you say that the relative velocity is nothing, but V 1 plus V 2 the addition of the two velocities.

So, it basically adds up the same thing the flux is also adding up here and second thing is that so, one is but then we are saying that the since A is these A is stationary and everything is calculated in a’s framework. So, the B is are approaching and once the encounter happens the then B is also depleting A is of course, also depleting, but then actually it is creating gradient for B and then actually more and more B will come.

Now, that is in somewhat it is an approximation because then the A should not be actually a initial it should be A bulk, but then as the A also vanishes the concentration of A also kind of drops. And it creates a gradient, but we are not considering the motion of A we are considering only the motion of B towards center which is basically at the center we have an A. So, to with these approximations this is a more or less correct expression for the diffusion limited reactions were actually we assume that every encounter will actually cause reaction.

So, the overall reaction is limited by the possibilities of the encounter that these two species actually come close together in a crowded environment because, they are coming in a zig zag path ways and they find A and B actually find the partner for each other and then they react. Now, in the next section we will be talking about the reaction between ions and what will actually move on with this particular treatment and then we will talk about what happens when actually you consider the electrostatics.

Thank you.