Advanced Chemical Thermodynamics & Kinetics
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Lecture - 33
Introduction to solution phase reactions dynamics 03

Hello everyone. So, we will continue our discussion on Reaction Dynamics in Solution, and remember that what we did in the last part is basically we considered the diffusion limited rate constant.

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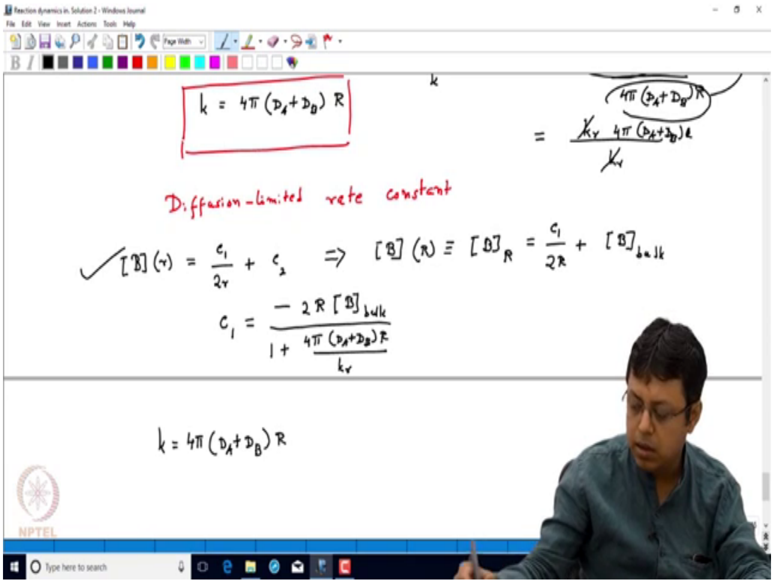

$$\boxed{k = 4\pi (D_A + D_B) R}$$

k

$$\frac{4\pi (D_A + D_B) R}{}$$

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

Diffusion-limited rate constant

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

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

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

And we derived an expression for the diffusion limited rate constant as write it rewriting it once again k is 4 pi D A plus D B, where D A and D B are the diffusion coefficients for the reactants A and B and times R, where R is basically the radius, the sum over the radius of the two reactant species. And this 4 pi capital R square is the volume over actually within which the reaction is occurring.

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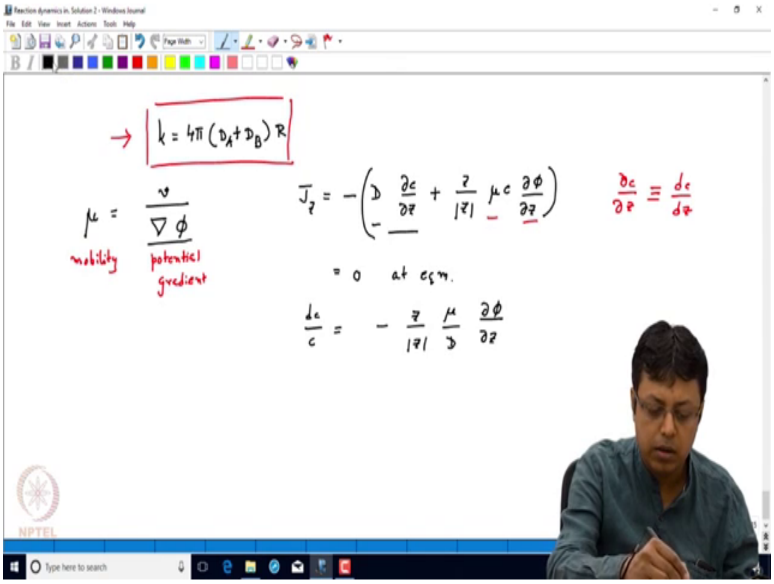

$$\rightarrow \boxed{k = 4\pi (D_A + D_B) R}$$

$$\mu = \frac{v}{\nabla \phi}$$

mobility potential gradient

$$J_z = -\left(D \frac{\partial c}{\partial z} + \frac{z}{|z|} \mu c \frac{\partial \phi}{\partial z}\right)$$

$$\frac{\partial c}{\partial z} \equiv \frac{dc}{dz}$$

$= 0$ at eqm.

$$\frac{dc}{c} = -\frac{z}{|z|} \frac{\mu}{D} \frac{\partial \phi}{\partial z}$$

Now, today what we are going to discuss is basically the reaction between ionic species. But for the moment we are not considering any particular ion like it is a positive or non-negative and or something like that. So, it can be between two opposite ions, it can be same similar ions, but similar ions you know that they will repel each other, but there can be reactions, you can make it more general in that sense that we will just keep the everything in terms of a electrostatic potential.

Meaning, so what we are going to do is that we are defining mobility which is which has been already introduced to you and we are writing the mobility. So, let me just write it also, this is mobility or the mobility of the ion. So, that mobility we are defining as the velocity of the ion divided by the potential gradient and in 3 dimensional the potential gradient is the gradient of a phi where phi is the potential. So, this is the potential gradient or the gradient of the potential.

So, what it means actually since the mobility is a constant the velocity is actually proportional to the potential gradient which makes sense, because if we have a higher potential gradient ions will move faster, on the charged species will move faster.

Now, if you remember in deriving this equation we started from the diffusion equation where we defined the flux as along some particular direction J z as a negative of the diffusion coefficient times the concentration gradient along z. But now we will have an extra component to it and that extra component we are writing it as I am writing it as plus z, where z is the charge of the ion divided by the modulus of z. So, basically it will dictate the sign of the time whether it is a positive ion and a negative ion and then multiplied by the ionic mobility, and times the concentration of the ion and times the potential gradient del phi del z. Now, I am now using instead of the gradient at the 3 dimensional gradient I am just using a one dimensional form.

So, basically mu into del phi del z this term. So, that is nothing but the velocity. So, you can actually see here. So, it is nothing but the c, the concentration times the velocity and times the charge species direction like whether it is moving in or moving out. So, you can actually take the negative sign within the outside the bracket.

And now these describe actually the total flux. The first part is a purely diffusive which does not contain any ionic contribution and the second part is the purely ionic contribution how the ions are moving against this potential gradient. So, the this part is the first part an stochastic movement, and the second part is basically an active motion of the ions.

Now, again the, at equilibrium we can actually assume that the net flux will be 0 and. So, it is basically you can set it to be 0 at equilibrium. So, this is exactly the same approach which we were doing and then we can rearrange the terms. So, you can see that I have to basically integrate the c dependent term and we could have instead of writing it as del c, del z, we could have writing it as dc, dz because there is no other coordinate we were just considering it as a one dimensional problem right now. So, it is identical to dc, dz. So, we can actually rearrange it. So, let us follow it. So, what we will have is I am keeping this term on the left hand side and then dividing it by c, so dc by c.

So, I will be left on the right hand side as a minus z by modulus of z, and then mu the c I have already taken on the other side and then I will have divided by the diffusion coefficient because there was a d here associated with dc by dz and then I will have del phi and I will have del z. So, del phi del z it into I will have dz. So, that will overall make it d phi. Again this potential also as I have written it as a variation of partial derivative it is nothing but d phi dz.

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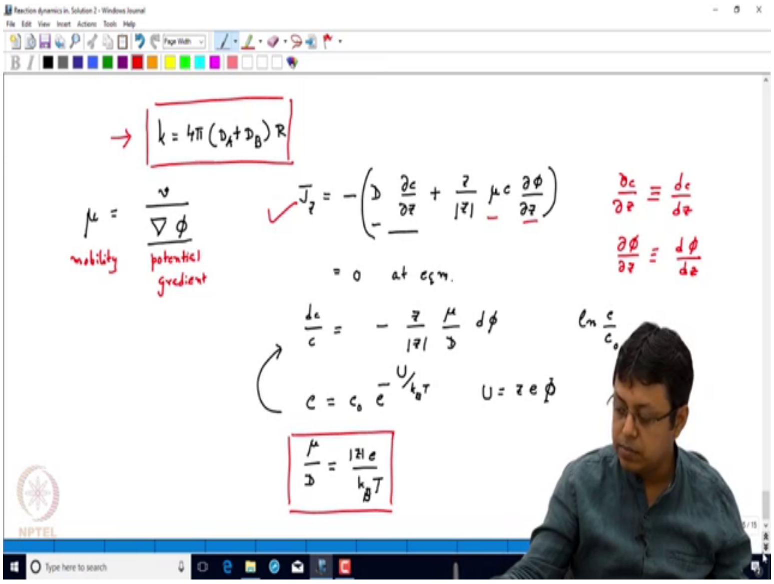

$$\boxed{k = 4\pi (D_A + D_B) R}$$

$$\mu = \frac{v}{\nabla \phi}$$

mobility

potential gradient

$$J_z = -\left(D \frac{\partial c}{\partial z} + \frac{z}{|z|} \mu c \frac{\partial \phi}{\partial z} \right)$$

$= 0$ at eqm.

$$\frac{\partial c}{\partial z} \equiv \frac{dc}{dz}$$

$$\frac{\partial \phi}{\partial z} \equiv \frac{d\phi}{dz}$$

$$\frac{dc}{c} = - \frac{z}{|z|} \frac{\mu}{D} d\phi$$

$\ln \frac{c}{c_0}$

$$c = c_0 e^{-U/k_BT} \qquad U = ze\phi$$

$$\boxed{\frac{\mu}{D} = \frac{|z| e}{k_B T}}$$

Now, we will integrate this equation. And the integration is again pretty straightforward in this case. So, z is a constant, mu is the mobility that is also constant and. So,, but before doing this integration we will just make some approximation. So, let us not integrate it in this way. So, let us see actually how, let us discuss how the integration should look like.

Now, as you can see it is dc by c. So, it will the integration will be some logarithmic integration ln c and then we can also put some initial condition that at phi equal to 0 the concentration is c 0. So, before attempting the solution let us assume that this solution what we are guessing that it will have some logarithmic solution something like say ln c, and if I put the initial condition that c 0 was the concentration at phi 0 and then on a my right hand side if I just remove the logarithm it will be c is equal to c 0 into e to the power something. And let us assume that it has and dependence, this concentration has a dependence which is something like a Boltzmann type.

In the sense that c is something like c 0 into e to the power minus some potential energy U which we do not know at this moment divided by k B T. Now, what is u? Now, U is the electrostatic potential and by definition U is nothing but if the it is a potential energy it is nothing but z times e is the fundamental charge and into the phi where phi is basically the electrostatic potential.

So, the potential energy is nothing but as you know that it is basically the how do you get the energy. So, if we bring the unit positive charge that is basically defined as the potential right, the forces which is felt in bringing the unit positive. So, we have to just multiply the charge with itself and then we will get the total potential energy. And then what we can do is that we can substitute this value into this equation, and if we do that you will get that mu by d is nothing but you can get an estimate of the diffusion connection of the diffusion coefficient with the mobility.

Because remember that one part is coming from the mobility of the electrostatic the other part is coming from the diffusion coefficient, and what we did is basically a kept a ratio of between them. Now, you can show it very easily. So, the way you show it is that you write c is c 0; e to the power of minus z e phi by k B T and then basically you can take the derivative ln c by c 0 and then just equate it. So, what you will get is dc by z and then you just equate left hand and with right hand, then you can easily figure out this equation.

And then the total flux, now becomes in terms of this whatever we have written here. So, you can rewrite this equation as, so let us follow the first equation about J z, the z component of the flux is nothing but minus d into del c del z; I can write it as right now dc, dz plus I had z by z magnitude of z and times mu c into d phi dz.

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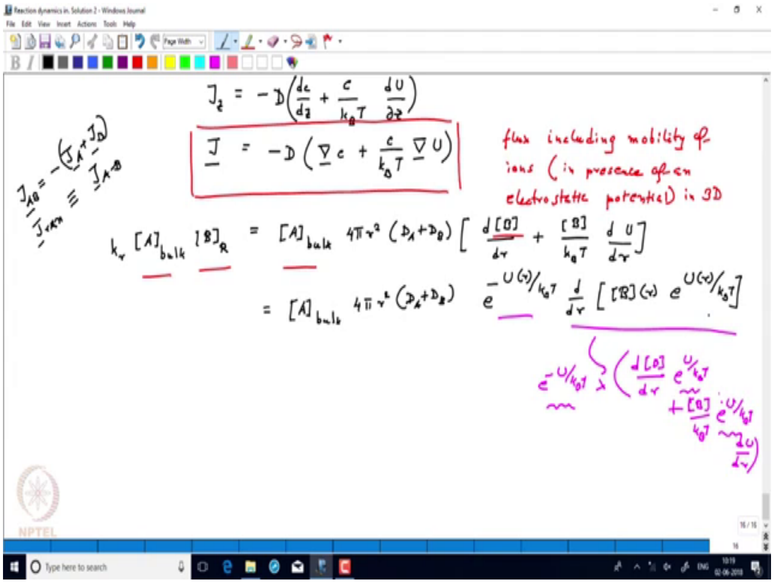

$$J_z = -D\left(\frac{dc}{dz} + \frac{c}{k_BT}\frac{dU}{\partial z}\right)$$

$$\boxed{\underline{J} = -D\left(\underline{\nabla} c + \frac{c}{k_BT}\underline{\nabla} U\right)}$$

flux including mobility of ions (in presence of an electrostatic potential) in 3D

$$J_{AB} = -(J_A + J_B) \equiv J_{A^B}$$

$$J_{rxn}$$

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

$$= [A]_{bulk}\, 4\pi r^2 (D_A + D_B)\, e^{\underline{-U(r)}/k_BT}\, \underline{\frac{d}{dr}\left[[B](r)\, e^{U(r)/k_BT}\right]}$$

$$e^{-U/k_BT}\Big\}\left(\frac{d[B]}{dr}e^{U/k_BT} + \frac{[B]}{k_BT}e^{U/k_BT}\frac{dU}{dr}\right)$$

Now, I have already given a value of mu by d. So, using that you can easily show it that it will be c by k B T and times we will have d U, dz where we have taken the diffusion coefficient common. So, this is the modified equation for the reactive for the flux of course, which is equivalent to the reactive flux that we are going to connect eventually. So, we can now say by analogy that actually this is the z component of the flux, but in reality the total vectorial flux will be something like minus D into instead of D dz it will be just the 3 dimensional gradient of the concentration plus we will have c by k B T and gradient of the potential.

And so this is a general equation for the flux including the effect of ionic mobility in 3D. So, flux for 3D or we can actually write it flux including mobility of ions which is in presence of a potential of an electrostatic potential in presence of an electrostatic potential which was phi, but we in this equation we have connected the phi with the potential energy which is U in 3, this is basically the 3D distribution.

Now, we can actually solve this equation. We have the flux equation and what we do if you go back and think about how we derived it, what we did is basically starting from this equation that the rate of product formation is nothing but equal to the reactive rate if you follow this equation times the bulk concentration of a times the B, local concentration of B at the reaction zone. And then it is multiplied by the J reaction, right now J reaction is equivalent to the J itself into 4 pi r square into A bulk and then all we are going to do is instead of writing this J as something like D A plus D B into this, we are going to actually include the electrostatic potentials effect and that is what we are going to do.

So, on my left hand side I will have the rate as k r, I am using the similar notation as we used in the last lecture a equilibrium. I think I was using instead of a equilibrium notation I was using the bulk notation because this is the bulk concentration of A and times the concentration of B, at a position r which is the position where the reaction is occurring and which is equal to A bulk times I will have 4 pi r square times I will have D A plus D B and then I will have, so this D remember this is a generalized D for one species for two species. So, we know that there will be a net flux because A is moving towards B and B is moving towards A.

So, instead of D, all the Ds will be replaced by D A plus D B and the flux we are writing it as if you remember that J A B we are writing it as minus of J A plus J B that way we were writing these are all vector quantities. And secondly, we have also used the fact that this J reaction is identical to the J A B and it is also diffusion limited. So, I will have two terms or the first term is the time derivative of the D B sorry the spatial derivative of B and which is the concentration of B how it varies with the radius means the distance from the central ion which is A. And plus I will have the B divided by k B T and times I have a potential which is d U, dz. So, this is the overall expression for this because remember that c is basically the concentration, instead of c I am just writing a B in third bracket that represents the concentration of a B.

Now, again ideally instead of d U dz, I should use a d U, dr and again I am not using the gradient sign here the reason being actually it is a gradient, but ultimately the gradient depends on only the radial coordinate not on the angular coordinates. Now, all we are left with is basically to rearrange and integrate this equation. So, what we c here right now is that we have an equation for B R and remember that this is basically a constant a concentration of B at the reaction zone. And then this is also constant A bulk, anywhere A bulk will be eliminated from both sides eventually and also I have a B and this B is nothing but the it is a variable, is basically a how the concentration is varying with the radial position as it as an we increase the distance from the central ion which is the D.

Now, we can actually rewrite the right hand side as this, so A bulk times 4 pi r square D A plus D B and then you look at it carefully I am just writing it as e to the power minus U r by k B T and then d dr of B, and again B is a function of r times e to the power U r by k B T. Now, you note here what we have done you can easily check it. So, if I take this derivative, this derivative if I do it. So, what I will get? I will get the first derivative as d B, d r and times I will have the second term e to the power U by k B T plus I will have I will keep the first function constant B and then a derivative of the second function which is basically 1 over k B T.

So, this k B T comes here into d U or let me just first do the exponentials derivative. So, it will be e to the power minus e to the power plus U by k B T times d U dr. So, now, we are multiplying it by e to the power minus k B T, if I just multiply it by e to the power minus U by k B T you can see that this and this cancels and also this term also gets cancelled. So, we are actually getting back our original equation. So, these are busy basically very clever way of writing the above equation.

So, ultimately what we are getting is now we are going to actually rewrite this equation the entire equation, because as you can see here is that I have a derivative of this entire quantity B times e to the power U r by k B T something like that. So, what I am going to do is basically divide both side by so dividing both sides by one is this thing on the A bulk because that will get cancelled A bulk times suppose I want to do the r square r integration on my left. So, I will also divide both sides by r squared.

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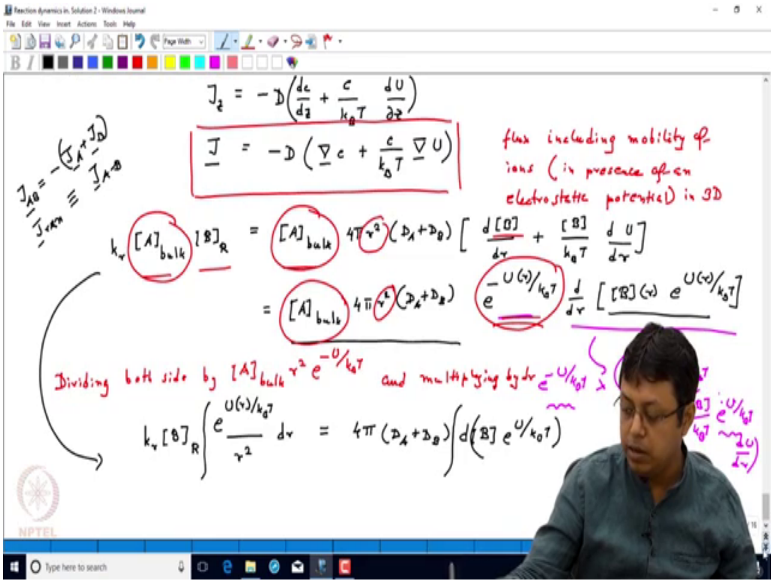

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flux including mobility of ions (in presence of an electrostatic potential) in 3D

$J_{AB} = -(J_A + J_B)$

$J_{rxn} \equiv J_{A\cdot B}$

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

$$= [A]_{bulk}\, 4\pi r^2 (D_A + D_B)\, e^{-U(r)/k_BT}\frac{d}{dr}\left[[B](r)\, e^{U(r)/k_BT}\right]$$

Dividing both side by $[A]_{bulk} r^2 e^{-U/k_BT}$ and multiplying by dr

$$k_r [B]_R \int \frac{e^{U(r)/k_BT}}{r^2}\, dr = 4\pi (D_A + D_B)\int d\left([B]\, e^{U/k_BT}\right)$$

And also I will I want to basically eliminate this term. So, into e to the power minus U by k B T and again U is a function of small r. And since I am doing the r integration on my left, so we have to multiplying a by multiplying by dr, so then what we will get is a very interesting expression is k r this small r is a reactive rate remember. So, A bulk will cancel.

So, I am getting from here. So, I will have B at R and then I will have I am divided by e to the power minus U by k B T. So, I will have e to the power plus U this is a function of r by k B T divided by I will have r square because I divided both sides by r square and also multiply dr and then I will have this line. So, follow carefully. So, I will have this thing is already got cancelled, and then the r square will also be removed and this part I have already will not be there. So, what I will have is 4 pi I will have D A by D B, D A plus D B and then I will have d.

Now, this entire expression let us have a look at it this integration actually you can keep it for the time being like this e to the power U by k B T this is total derivative. Now, we can actually straightforward way integrate it, but the problem here is that if I just want to integrate it remember that k r is a constant, B R is also a constant. If I integrate it like this, now the left hand side integration I cannot do immediately because I need to know what is the form of U of r because I do not know yet how the potential varies with the distance. So, since I do not know this form I can simply say that I am just keeping it as constant and again the limits I am setting when r is equal to R, I know that B is nothing but equal to B R and we will see it actually. So, let us not write the limit right now, because we will be evaluating it at small r equal to R and small r is equal to infinity and you will see what we will get the right hand side.

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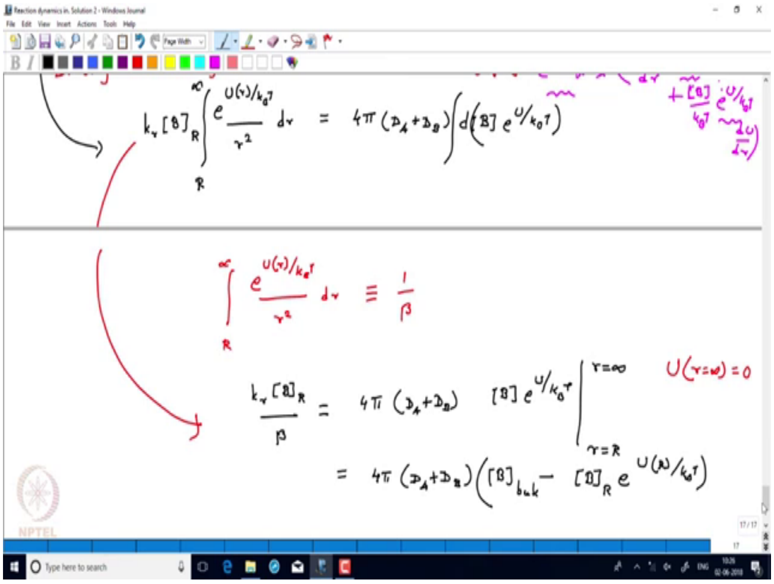

$$k_r[B]_R \int_R^{\infty} \frac{e^{U(r)/k_BT}}{r^2}\,dr = 4\pi(D_A+D_B)\int d\left([B]\,e^{U/k_BT}\right)$$

$$+\frac{[B]}{k_BT}e^{U/k_BT}\frac{dU}{dr}$$

$$\int_R^{\infty} \frac{e^{U(r)/k_BT}}{r^2}\,dr \equiv \frac{1}{\beta}$$

$$\frac{k_r[B]_R}{\beta} = 4\pi(D_A+D_B)\;[B]\,e^{U/k_BT}\Big|_{r=R}^{r=\infty} \qquad U(r=\infty)=0$$

$$= 4\pi(D_A+D_B)\left([B]_{bulk} - [B]_R\,e^{U(R)/k_BT}\right)$$

So, this integration I am defining it to be a new quantity and suppose I call it this integration integral as capital R to infinity e to the power U r by k B T divided by r squared d r. So, remember that it depends on the nature of the potential and the potential energy we just wrote. But we do not know explicit form of a U how it varies with a small r. So, that is why you cannot evaluate it and I am just writing it as 1 over beta. So, we just keep it as 1 over beta. So, if we use that then this equation becomes let me just rewrite it.

So, I will just write it as k r, B at position r divided by beta. So, that is equal to 4 pi D A plus D B and then I have to evaluate this integral, but this is just a straightforward integral, but I am writing it as B into e to the power U by k B T evaluated at r is equal to small r is equal to r and small r is equal to infinity. Now, that we can easily figure out D A plus D B and then it is very easy to figure out, now to see here that when and the upper limit you first look at when r is equal to infinity we know that B is nothing but equal to the bulk concentration and the lower limit and again the U infinity also you at r equal to infinity that also there taken to be 0 because it is basically the potential energy at infinite distance. So, there when there is no influence of the first charge A and then also the at point r is equal to capital R. So, we know that this is nothing but B at R and I will have e to the power U at r divided by k B T.

So, that way actually you can write it and then we can actually rearrange the terms. So, we are done with the integration. So, let us just rearrange it.

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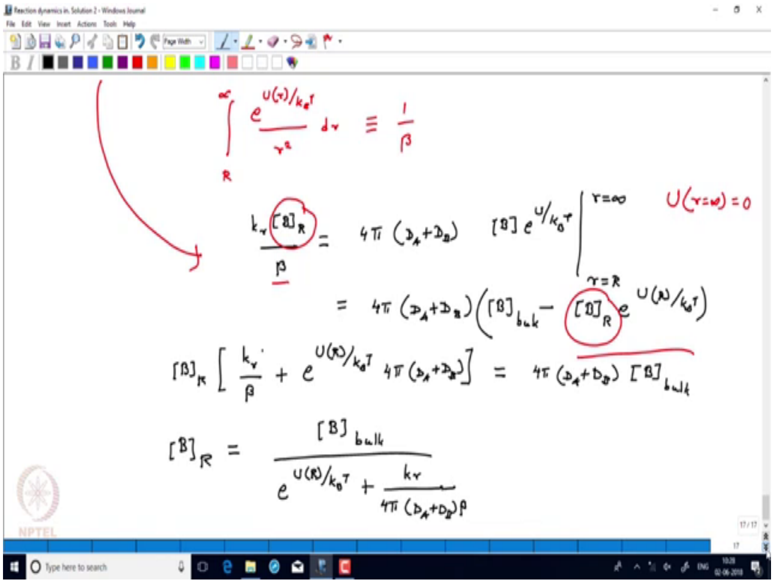

$$\int_R^{\infty} \frac{e^{U(r)/k_BT}}{r^2}\,dr \equiv \frac{1}{\beta}$$

$$\frac{k_r \boxed{[B]_R}}{\beta} = 4\pi(D_A+D_B)\;[B]\,e^{U/k_BT}\Big|_{r=R}^{r=\infty} \qquad U(r=\infty)=0$$

$$= 4\pi(D_A+D_B)\left([B]_{bulk} - \boxed{[B]_R}\,e^{U(R)/k_BT}\right)$$

$$[B]_R\left[\frac{k_r}{\beta} + e^{U(R)/k_BT}\,4\pi(D_A+D_B)\right] = 4\pi(D_A+D_B)\,[B]_{bulk}$$

$$[B]_R = \frac{[B]_{bulk}}{e^{U(R)/k_BT} + \frac{k_r}{4\pi(D_A+D_B)\beta}}$$

So, we will have B R, B at in position r times I will have k r divided by beta. So, I am basically taking this B R common just like we did in the last part also, but last time, but we did not have this equation that time because that is the potential dependent that depends on this electrostatic position. Also you did not have the beta that then will come to it. And then what we have inside is I will have a plus sign because I am bringing this term on the right hand side to the left hand side.

So, I will have e to the power U at R divided by k B T. So, this is not a variable this is basically a constant U at R. And multiply by I have 4 pi D A plus D B that is always there and that is equal to 4 pi D A plus D B times I have the B bulk. So, now, we can easily see what will be the value of B at R. So, that will be nothing but B at bulk and times the 4 pi D A plus D B, but we can actually divide the numerator and denominator again by 4 pi D A plus D B. And you know that how to do it and then I will have two terms basically one will be the I am just writing the second term in the denominator e to the power U of R divided by k B T plus I will have k r divided by 4 pi D A plus D B into beta. So, remember that all we have to evaluate is the rate.

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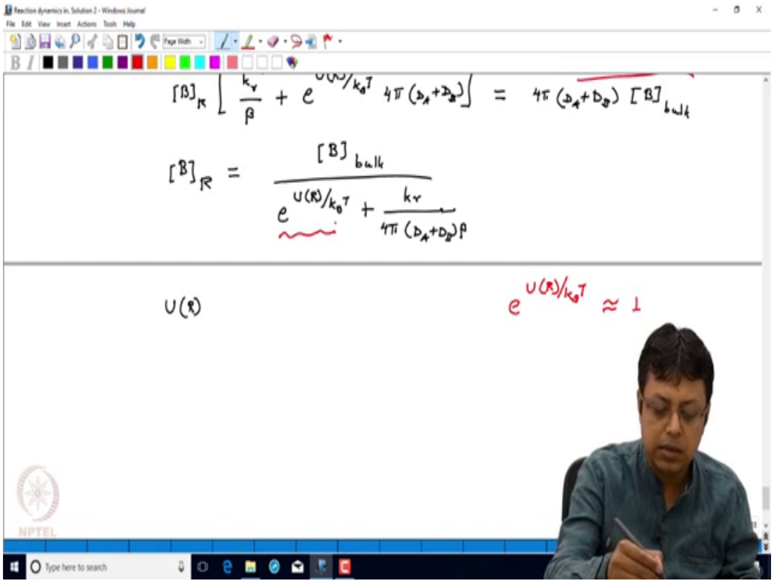

$$[B]_R \left[\frac{k_r}{\beta} + e^{U(R)/k_BT}\, 4\pi (D_A + D_B) \right] = 4\pi (D_A + D_B)\, [B]_{bulk}$$

$$[B]_R = \frac{[B]_{bulk}}{e^{U(R)/k_BT} + \frac{k_r}{4\pi (D_A + D_B)\beta}}$$

$U(R)$

$$e^{U(R)/k_BT} \approx 1$$

So, basically what we can say that U of R or meaning actually the potential at a reactive zone it is basically will be very small. Why? The reason is actually you can think about it at infinitely it is 0.

Now, when if we assume that the two ions are in contact then actually when they are far apart then there is a potential acting on them. So, there is a huge potential energy between them, but when they are in contact they are kind of in an equilibrium position. So, then actually that family will be very small, and usually we can actually ignore that value in a sense that we have an exponential of e to the power we have e to the power U

R by k B T, and since that value is very small we can actually approximate it the exponential to be truncated in the first term only. So, we are just using it as one it.

So, now, do not get confused that when I am keeping the r equal to infinity that you of art was basically 0. Now, as I am in brining it together closer to the second and the potential is increasing, increasing in the negative sense, but when the ions are in contact then I can assume that that potential has gone into its minimum position. So, that is why you are ignoring it and we are saying that compared to k B T it is small. So, that is the entire thing.

So, then I can actually approximate U R since it is very small, and then we can just remove this thing and you can just write it instead of this entire term you can actually write it as 1, and then I as we know that the rate of product formation the dp dt.

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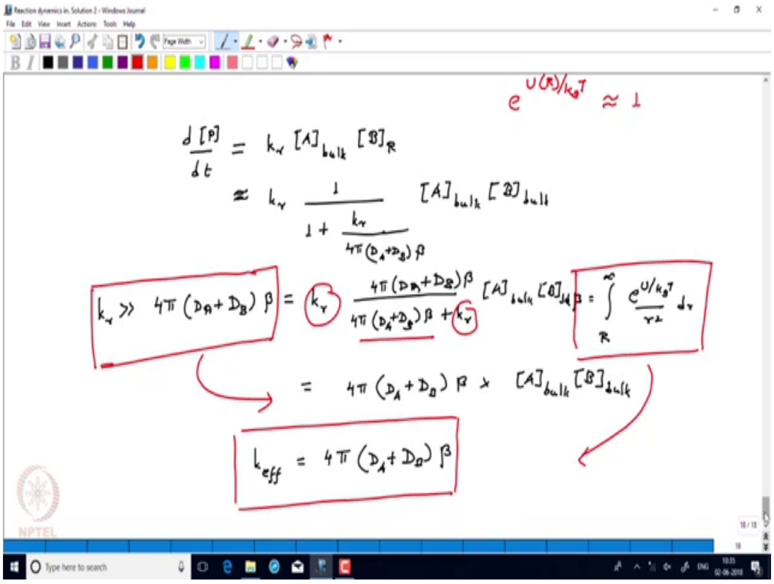

$$e^{U(R)/k_BT} \approx 1$$

$$\frac{d[P]}{dt} = k_r [A]_{bulk} [B]_R$$

$$\approx k_r \frac{1}{1 + \frac{k_r}{4\pi(D_A+D_B)\beta}} [A]_{bulk} [B]_{bulk}$$

$$\boxed{k_r \gg 4\pi(D_A+D_B)\beta} = k_r \frac{4\pi(D_A+D_B)\beta}{\underline{4\pi(D_A+D_B)\beta} + k_r} [A]_{bulk} [B]_{bulk} \quad \boxed{\beta = \int_R^\infty \frac{e^{U/k_BT}}{r^2} dr}$$

$$= 4\pi(D_A+D_B)\beta \times [A]_{bulk} [B]_{bulk}$$

$$\boxed{k_{eff} = 4\pi(D_A+D_B)\beta}$$

So, this is following the same kind of notation we have been using dp dt that under this approximation becomes, so the B bulk is nothing but if we go back what was the dp dt formula. So, it was this it is basically k r times A bulk into B R. So, let us write it is k r. So, up to this point this is the exact thing. So, this is the under diffusion limited, right. So, you are going to approximate it again, so k r into A bulk times B at a position R. So, B at a position R that is what we have evaluated, so I will have k r times A bulk or A bulk we can actually write it later. So, you have 1 over.

So, this term I have taken to be 1, I will have k r by 4 pi D A plus D B into beta and times A bulk into B bulk. So, these are the bulk concentration. And this was an approximation because here we have made the e to the power term to be 1. And then again we can approximate that this reactive rate of the rate of the second step where actually the products are being formed. So, every contact or every encounter is giving me reaction then that will be much higher than this diffusion limited term D A plus D B which also contains the term which is beta and remember that beta is coming from this integration that I have e to the power U by k B T divided by r square dr that integration, where r is going from the contact distance to infinite distance.

And if I approximate that then you know how to do it what we get from here is I will have I am just expanding it is k r, then I will have 4 pi D A plus D B into beta plus k r and divided by 4 pi D A plus D B. So, that I am moving into the numerator D A plus D B and then I have A bulk into B bulk and then I can say is that this term using this condition. So, you can now write including beta.

So, you can now write that this term is much smaller than this care term. So, you can ignore it and moment to ignore it this k r gets cancelled with this k r and then we get the final expression as the rate of product formation is basically 4 pi there will be beta here D A plus D B into beta times A bulk into B bulk. So, what we see here the effective rate constant as before is nothing but 4 pi D A plus D B, but there is an additional term which is the beta and that is how it is basically getting included. And that is a beautiful way of showing it that although this beta has a very complicated expression because we do not we did not included it, and we just said that it is basically the variation of the potential and how it depends on this integration on the variation of the potential.

We just note it term which is beta, and the only difference we see from the diffusion under the diffusion limit between the species which are non-ionic or non-charged and the species which are charged is this small difference which is the beta. And interestingly, so earlier as you can see that the earlier expression content an r it was a 4 pi D A plus D B into r. Now, if you look at it. So, the dimension wise it should be the dimension of capital R. So, let me just rewrite the two equations.

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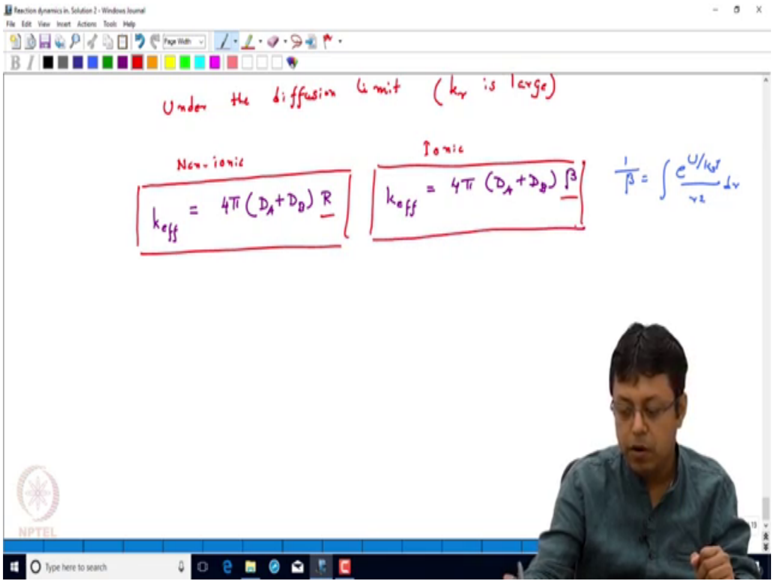

Under the diffusion limit (k_r is large)

Non-ionic

$$\boxed{k_{eff} = 4\pi (D_A+D_B) \underline{R}}$$

Ionic

$$\boxed{k_{eff} = 4\pi (D_A+D_B) \underline{\beta}}$$

$$\frac{1}{\beta} = \int \frac{e^{U/k_BT}}{r^2} dr$$

So, for under the diffusion limit, so under the diffusion limit which means the limiting step is the diffusion of the encounter, encounter itself because once the encounter every encounter is giving me the reaction which means that k r is large compared to the other terms. And then for non-charge species or non-ionic species versus the ionic species the effective rate in one case we are getting 4 pi D A plus D B which is the addition of the diffusion coefficient of the two spaces times R. And in the other case we are getting k effective is 4 pi D A plus D B times beta.

Now, I know that R is basically the contact distance and where this beta is nothing but the integral e to the power U by k B T, n divided by r squared here. Now, if you look at it carefully it is basically e to the power U by k B T is a number and then dr by r square, so e to e to the power U by k B T will be basically unitless and dr by r square has a dimension of basically the same dimension the contacts the r dimension. So, dimension wise they are still the same. And so remember that we wrote it as a 1 over beta, not beta. So, it should also write it here. So, that was beta inverse it is 1 over beta.

And then so beta has a dimension of 1 over r on over length. So, beta inverse as a dimension of one over beta has a dimension of 1 over length. So, beta has a dimension of length. So, thus we see the only difference coming between these two equations is here and where in one case we have included the electrostatic protection there and the other case it is just simply the distance of the contact pairs center to center distance.

So, thus we have shown that how one can actually mathematically develop the effective rate constant under the diffusion limit for ionic and non-ionic spaces. So, we just conclude our discussion on the reaction dynamics in solution here, and then we will basically summarize the entire portion that we have covered.

Thank you.