Advanced Chemical Thermodynamic & Kinetics
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Lecture – 13
Transport Phenomena – 3

So, let us now check how this equation which we rewrite for the general transport behavior takes the form for individual cases. Let us first talk about the heat transfer.

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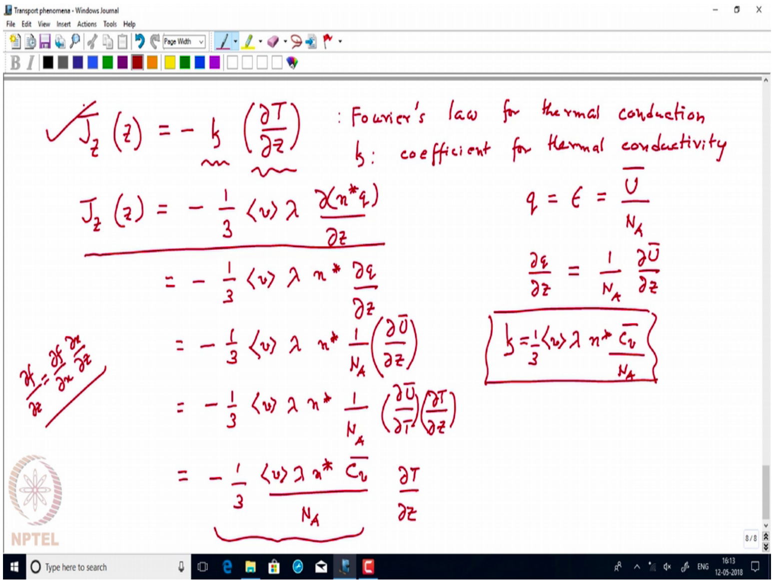

$$\checkmark\; J_z(z) = -\underset{\sim}{\kappa}\underset{\sim}{\left(\frac{\partial T}{\partial z}\right)}$$

: Fourier's law for thermal conduction

κ: coefficient for thermal conductivity

$$J_z(z) = -\frac{1}{3}\langle v\rangle\lambda\frac{\partial(n^*q)}{\partial z}$$

$$= -\frac{1}{3}\langle v\rangle\lambda n^*\frac{\partial q}{\partial z}$$

$$= -\frac{1}{3}\langle v\rangle\lambda n^*\frac{1}{N_A}\left(\frac{\partial\bar{U}}{\partial z}\right)$$

$$= -\frac{1}{3}\langle v\rangle\lambda n^*\frac{1}{N_A}\left(\frac{\partial\bar{U}}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right)$$

$$= \underbrace{-\frac{1}{3}\frac{\langle v\rangle\lambda n^*\bar{C_v}}{N_A}}\frac{\partial T}{\partial z}$$

$$\frac{\partial f}{\partial z} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial z}$$

$$q = \epsilon = \frac{\bar{U}}{N_A}$$

$$\frac{\partial q}{\partial z} = \frac{1}{N_A}\frac{\partial\bar{U}}{\partial z}$$

$$\boxed{\kappa = \frac{1}{3}\langle v\rangle\lambda n^*\frac{\bar{C_v}}{N_A}}$$

Now, the equation for heat transfer of the flux for heat transfer which is dependent on z is given by Fourier's law and we know that Fourier's law is basically the flux will be dependent on the temperature gradient. So, I will have some term like del T, del z, special gradient of temperature and times the constant with the negative sign and that constant we write as kappa. So, this is the Fourier's law for heat conduction, where kappa is known as the coefficient for thermal conductivity.

Now, using the relationship which we developed for J z the question is, how can we actually get mathematical form or some formula for kappa? Now, let me just rewrite the value of J z. So, it is one third minus one third average velocity times the mean free path and times the number density multiplied by the quantity that is being transferred and divided by special derivative.

Now, here what is q? Now, q is basically the amount of energy, because it is a heat transport carried by every molecule. So, it is a basically heat transport per molecule. So, q is nothing, but suppose per molecule, I am just writing it as epsilon which means it is nothing, but the total energy.

So, suppose if U is the average energy carried by one (Refer Time: 0:2:26) or U bar or something like you can write, it is U bar divided by the, Avogadro number. So, that will be the energy carried by each molecule on average. Also, we see that this derivative this partial derivative with respect to z, the reason we are writing partial derivative, because it can also vary temporally and we will see a special case where actually we have, have the quantity which is varying not only specially, but also (Refer Time: 0:2;56) whenever we discuss diffusion.

So, in this case the instant the number density usually does not change, because when you con consider heat conduction. So, it is a conduction phenomena, not the convection phenomena. So, for thermal conduction, so it is a Fick's law for thermal conduction. So, conduction by definition means that the molecules or the particles does not move rather, actually in the molecular which will be deal the (Refer Time: 0:3:25) and at the same position and they transfer the heat to the neighboring molecule and that is how the heat conduction works. So, the instead of the number density does not change with transistor change especially. So, there is no density gradient.

So, I, we can actually take it outside the differential and. So, it will be nothing, but del q del z as we said q is nothing, but average energy or you can say internal energy. So, del q del z will be nothing, but 1 over N A del U del z. Now, you see here you can actually replace it minus one third v average lambda n star and then one over N A.

We can write del U average del z, but see here that we have in the original definition of Fourier's law, del T del z. So, we have now del U del z, so we can easily convert it. So, we will take a del U del t we can write the differential like this we know that if I have a function like this let us say del f del z, I can actually write it as del f del x into del x del z and we are going to actually use the same formula. So, lambda into n star 1 over Avogadro number and we are writing it as del U del T into del T del z.

Now, you see what is this quantity del U del T, it is basically change in internal energy per unit temperature, so this is also internal energy per mole. So, this is nothing, but the heat capacity and heat capacity per mole, because we said that U, it is U bar, it is average energy per mole. So, what we get is nothing, but 1 minus one third v average lambda n star C v bar by C v bar I mean that heat capacity per mole divided by the Avogadro number into del T del z and we see this entire quantity is kappa.

So, kappa is nothing, but average velocity times there is a one third, one third of average velocity times the mean free path times the number density times the C v bar divided by the Avogadro number. So, thus we see that how we can get a very handy expression for the coefficient of thermal conductivity using the fundamental relation that we derived for any transport phenomena.

And, now we will see for thermal conductivity the Fourier's law is there if this is a phenomenological law and similarly for say mass flow which is diffusion we are going to discuss a diffusion later. First we can actually discuss let us say, viscosity. Now, for viscosity there is a relation and it is known as Newton's law for this viscosity.

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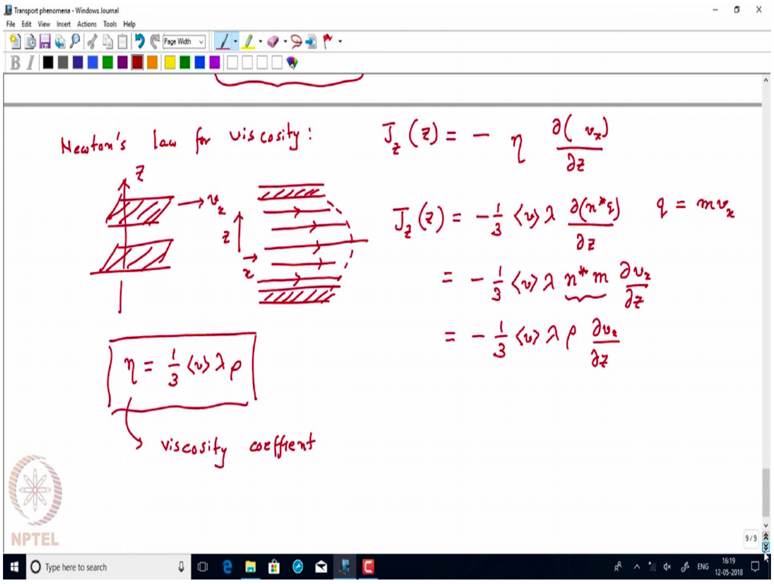

Newton's law for viscosity:

$$J_z(z) = -\eta \frac{\partial(v_x)}{\partial z}$$

$$J_z(z) = -\frac{1}{3}\langle v\rangle \lambda \frac{\partial(n^* q)}{\partial z} \qquad q = mv_x$$

$$= -\frac{1}{3}\langle v\rangle \lambda \underbrace{n^* m}\frac{\partial v_x}{\partial z}$$

$$= -\frac{1}{3}\langle v\rangle \lambda \rho \frac{\partial v_x}{\partial z}$$

$$\boxed{\eta = \frac{1}{3}\langle v\rangle \lambda \rho}$$

→ viscosity coeffient

So, let us see the formula, Newton's law for viscosity. Now, before I write down the law, let me actually tell you what, what is transferred in when you talk about viscosity, suppose again along z axis I have several layers which are actually separated by the distance which is equivalent to the mean free path now the question is. So, this is along z axis. Now we also have molecules moving in the x and y direction.

Now let us say this is x direction, now what is transferred across the z direction or along the z direction is the x component momentum. So, that is a little bit difficult to perceive in the sense that it is the x component momentum that is being transferred. So, what we say here is that, we are talking about a gradient along z axis.

So, it will be still a partial derivative with respect to z, but the quantity here is that how the v x is changing and if you remember that if that changes, like suppose a fluid is flowing you have seen this kind of picture probably and then we say that due to friction suppose this is the wall of the container and then we say that the layers of the fluid which are close by here will have a very slow velocity than the layer, which are at the center.

So, the sometimes actually it is written like the, fluid actually flows like this, the reason is, just because of the fact that the x component momentum has a gradient along z. So, this is z and this is x. What is the Newton's law? So, Newton's law is again some flux which is the viscosity equation which is a function of z and that would be negative of the gradient of the momentum which is nothing, but m into v x, m is the mass for each particle, del z and times you have eta.

So, eta is known as the coefficient of thermal coefficient of viscosity. Now, although it is a momentum graded usually in Newton's equation the mass is not written. So, we will have to introduce a quantity mass and then we can easily connect it to this equation and then figure out what is eta in a similar way.

Now, let us just write it what is the z? It is rather straight forward the viscosity equation. So, it, it will be nothing, but in our notation it is minus one third you can go back and have a see have a look. So, it is minus one third v average lambda and then you had del n star and q and then, we can just write it like this del n star into q and del z.

Now when the fluid is flowing in this case also what is happening at the layers are basically parallel to each other and that is why there is no turbulence in the flow and these kind of liquids are known as Newtonian fluids and then what happens here is that as the fluid flows only the momentum gets transferred. So, we can say that as before just like the thermal conductivity here also the number of particles are not changing. So, that n star we can actually take it out of the differentiation also in this case q is nothing, but the momentum so, m into v x, the x component of the momentum.

So, we can readily see that it will be minus one third v average lambda and I have n star and then it is del q del z, but remember that q is also m into v x. So, ultimately the m also comes out because it is just a constant, it is a mass of the mass of each particle. So, you have del v x del z. Now we can easily compare, but before comparing I will just make one more simplification. So, it is minus one third v average lambda and then you see that n star into m, n star is number density times mass, so that we write as rho or basically the mass density. So, that is why I did not use the rho notation for n star into q in the earlier I mean earlier pages.

So, now we can compare and you can get a expression for the coefficient of viscosity or viscosity coefficient. It is nothing, but one third v average and you have lambda into rho. So, that we get another expression for another quantity. So, which is the coefficient for a viscosity or a viscosity coefficient.

So, this is a viscosity coefficient. Now, we will talk about diffusion, now diffusion is very interesting and it, it is a very- very well studied a phenomena again the, what the treatment we are doing for diffusion is a very very simplified phenomenological description. Now for diffusion also just like, for thermal conductivity we had Fourier's law, for viscosity we had our momentum transfer we had Newton's law, for diffusion we have Fick's law.

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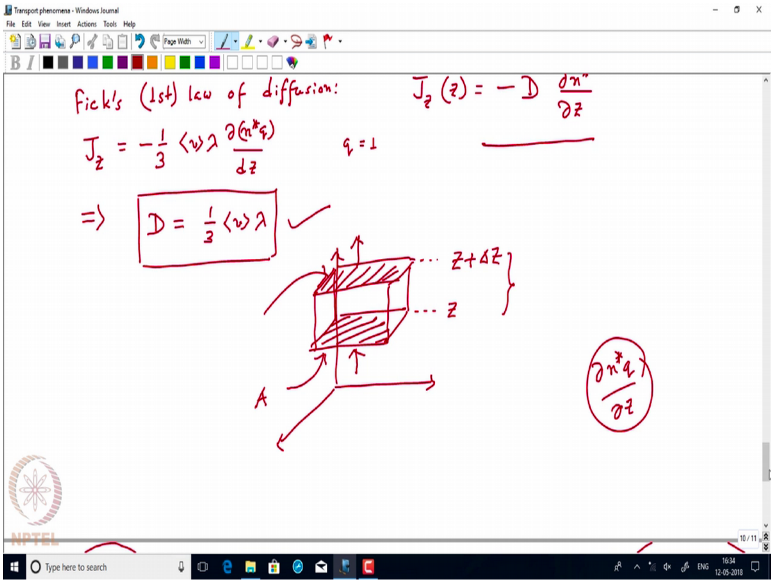

Fick's (1st) law of diffusion:

$$J_z(z) = -D\frac{\partial n^*}{\partial z}$$

$$J_z = -\frac{1}{3}\langle v\rangle\lambda\frac{\partial(n^*q)}{dz} \qquad q=1$$

$$\Rightarrow \boxed{D = \frac{1}{3}\langle v\rangle\lambda}$$

$$\frac{\partial n^* q}{\partial z}$$

And this law will first write it as a instead of calling it as a Fick's law will call it as a Fick's first law of diffusion. There is a reason why I am calling it as a first law of diffusion. Sometimes, sometimes we write it as a Fick's law of diffusion, sometimes we write it as a Fick's first law of diffusion.

So, that says the quantity in this case the flux which is basically the particles itself that is equivalent to the concentration gradient. Now, this is a pretty straightforward in this case, because if you just compare with our generalized equation which is minus one-third v average lambda del n star q del z and remember that in this case q is just nothing q is 1, because it is the particles itself how the n star is changing. So, you can readily figure out what is a D and coeffi diffusion coefficient comes out to be one third v average into lambda which is a very very straightforward.

Now, the interesting situation will happen when we say that this quantity which is they said. So, that also is varying which time why this happens, because among all the examples we told so far this is the only example where we talked about the n star itself has a gradient. So, basically and you the particles are basically moving or the molecules are moving Now we can think that as suppose I had a high concentration region and I have a low concentration region and particles are moving from high concentration to low concentration.

Now, what will happen over time is that as the particles are being moved the high concentration or the concentration in the high concentration region will fall down and the concentration in the low concentration region will increase. So, basically this del n star del z that will be time dependent itself. So, n star has a time dependent or the basically the concentration itself has a time dependence.

Now how will you incorporate this time dependence, now there is a very easy way to incorporate it suppose again we will consider two layers here, suppose this is one layer which is let us say at a position along z arbitrarily, I am calling it as z and there is another layer which is at position let us say z plus delta z.

Now, the question we are asking is that how many molecules are basically accumulating how that how this n star is changing with time that we can easily calculate by considering what is the net flux basically changing for the bottom one and net flux changing from the top one, and then if we take the difference from that actually we can calculate how many molecules are getting accumulated in this region in this volume, which I have shown as a rectangular volume.

So, now the thing is that that you can easily calculate. So, how do you calculate it, let us do it very systematically.

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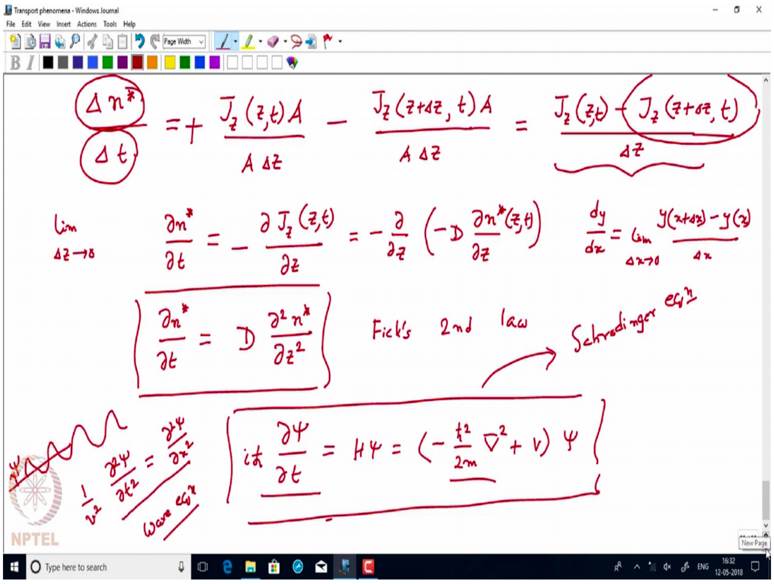

$$\frac{\boxed{\Delta n^*}}{\boxed{\Delta t}} = + \frac{J_z(z,t)A}{A\Delta z} - \frac{J_z(z+\Delta z,t)A}{A\Delta z} = \underbrace{\frac{J_z(z,t) - J_z(z+\Delta z,t)}{\Delta z}}$$

$$\lim_{\Delta z \to 0} \quad \frac{\partial n^*}{\partial t} = - \frac{\partial J_z(z,t)}{\partial z} = - \frac{\partial}{\partial z}\left(-D\frac{\partial n^*(z,t)}{\partial z}\right) \qquad \frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{y(x+\Delta x) - y(x)}{\Delta x}$$

$$\boxed{\frac{\partial n^*}{\partial t} = D\frac{\partial^2 n^*}{\partial z^2}}$$

Fick's 2nd law

$\rightarrow$ Schrodinger eqn

$$\frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2} = \frac{\partial^2 \psi}{\partial x^2}$$

Wave eqn

$$\boxed{i\hbar\frac{\partial \psi}{\partial t} = H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi}$$

So, let us say what I am saying here is that I want to calculate the delta n which is the delta n star, because we are using n star notation per unit time, now what that it will, what it will be. So, suppose in this particular volume now again, so instead remember it is a density.

So, I have to divide again I will first calculate, suppose the surface has some area, suppose the area is A, for this as well as for this, the area is A and then what we are going to calculate, we know the flux of flux is number of molecules changing per unit area per unit time.

So, suppose in delta t time the flux basically changes by this amount. So, right now I am writing z t as a function of both z as well as t and if this is the flux the number of molecules which are entering this area. So, per unit time it will be nothing, but times the cross sectional area because per unit time is already there. So, what we are going to calculate is changing the density per unit time.

So, this is basically the amount which is being get and divided, we also have to divide it by the volume. Now the volume is nothing, but a times this length and this length is a z plus delta z minus z which is delta z. So, this is the number of molecules which are entering per unit time, because a per unit area we have multiplied here and then I have to also make sure that number of molecules are also leaving through this surface, which is the surface, which is located at z plus delta z, but there the flux is, at is slightly different and at time t and into if I just, multiply the area. So, that will be the number of molecules leaving that surface part unit type, because I am multiplied by already the area.

So, then if I divide by the volume, so that is basically the number of molecules leaving this total volume, so that you can easily re organize and you can see that this a cancels in the numerator and denominator. So, what will be left to it, is basically the flux at z, sorry it will be flux at z and divided minus flux at z plus delta z divided by delta z.

Now, of course, you can now approximate that these delta z which we have chosen is much, much small, so in the sense that the limit delta z tends to zero. Now this quantity becomes a, by definition its basically the derivative of the flux with respect to the position and also to write it consistently we are writing the z, sorry z as a function of z the position as well as time here.

So, in that limit we can write that this change which we calculated is nothing, but the differential change per unit time is basically the time derivative of the concentration and that is nothing, but the special derivative of the flux.

Now if you note carefully that by definition suppose what is definition of d y d x, we just write it that it is the value of y at x plus delta x minus value of y at x divided by delta x in the limit delta x tends to 0. In the center can you see that there is a negative sign, because I am talking about z at a position z plus delta z, but with a negative sign. So, it should be there should be a negative sign here, but we know that this thing is nothing, but the negative gradient special gradient of this quantity J, but J for J already we have the Fick's first law which is nothing, but this, so you already know.

So, let us just put it back, so what we will have is that there is a minus D into del n star del z, n star depends on z as well as t, we are just writing it there very explicit, so what we get ultimately the time derivative of the particle density is equal to the second derivative of the particle density and this is basically the second derivative in space. So, this equation of this law is known as Fick’s second law of diffusion.

So, Fick’s first law actually talks about connects actually the coefficient of viscosity, I mean basically says the flux as a function of spatial gradient, but as time progresses the flux itself changes because the concentration gradient and the concentration itself is changing with time, because as the molecules move the concentration must change with time and so, the concentration gradient changes which means the flux itself changes and so, to incorporate that we figured out it is nothing, but the very nice equation that the concentration gradient with respect to time is nothing, but the second derivative of the concentration with respect to space.

Now, this is a very important equation in hydrodynamics and it has a lot of like applications, and one interesting analogy although this has nothing to do with this course is that the time dependent Schrodinger equation, which is actually the Schrodinger equation. Schrodinger equation means it is a time dependence Schrodinger equation.

So, when you write it you will see that the time derivative of the wave function is basically the gradient of the wave function. So, it is basically the kinetic energy and potential energy and kinetic energy has if you write it more explicitly. So, it is basically the Hamiltonian, and then you can write the Hamiltonian as minus H bar squared by twice m and del squared. Now del square is nothing, but the second derivative with respect to space and some potential energy acting on psi.

Now, if you look at this part like the on left hand side I have a time derivative and on right hand side I have actually double derivative with respect to space. So, that is why it is; of course, known as a Schrodinger equation, but Schrodinger equation is not exactly an wave equation, because what you do in wave equation when you are talk about suppose you just take a classical sinusoidal wave, and if you talk about the amplitude as say psi you will figure out that if you do the space derivative and a time derivative and use the definition of the velocity of the wave, then you will find that that wave equation will have something like del a H del to psi del t 2 will be equal to del 2 psi del x 2 with some production and constant it will be one over v square in this case yes.

So, v into x, yes, so that that is how it will come, but or it will be the one over v square in the other side, so it is a time derivative. So, then what you see here is a very interesting thing that here actually the on the either side we have double derivative in time and space.

So, this is the wave equation, but Schrodinger equation is actually strictly speaking, although it is a wave mechanics, because we talked about the wave particle duality and particles also have wave nature and from that it the interacting stemmed, but I mean like mathematically the Schrodinger equation is more close to the fixed second law, where actually the first derivative in time connects it to the second derivative in space. So, so this is just to give you a feeling like how things are all the way talking about very different physics here, but how things are connected.

So, so far whatever we have done is, basically let me go back we derive an equation for the generalized transport and then using this equation we said that we can always define a flux that is the most important quantity and this flunks depending on the particular phenomena, you are describing if the phenomena can be viscosity, the phenomena can the diffusion, the phenomena can be thermal conductivity and you can actually get a coefficient phenomenologically and using the analytical expression that, we derived you can actually get a mathematical formula for those coefficients; like we derived it for the viscosity coefficient, like we derived it for the thermal coefficient kappa and also we derived it for the diffusion coefficient and particularly for diffusion. We found that the this quantity that del n star into q del t the n star itself sorry del z the n star itself is changing here.

So, what it means that the as it changes especially things are moving from one side to another side which means over time also you will have dynamics and that is what we figured out here and we found that the very important relation that the first derivative of the concentration with respect to time is nothing, but the second derivative of the concentration in space.

So, we will stop the discussion here and in the next section we will be talking about the transport properties of ions which is slightly which we will use slightly different treatment there, because for ions there are a lot of electrostatics involved and then you whatever we have studied this diffusion coefficient of thermal conductivity although thermal conductivity is not very necessary for our discussion and viscosity. So, particularly diffusion those will be important when we will discuss the reaction dynamics in solution.

So, those things will be useful and there actually we will also talk about a little bit about the reaction between ions using the conductivity of the ionic, not ionic conductivity, its basically transport of ions, a movement of ions in solution and also we will see at the reaction dynamics section. We will discuss about the electron transfer reaction, but from a very different point of view from the potential energy surface point of view which is nothing, but Marcus theory of electron transfer.