Mathematics for Chemistry
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Lecture - 15

We have discussed first order differential equations and the techniques that we used to solve them. And we have also discussed the idea of a system of first order differential equations. And now we will put our ideas in to practice, and we will try to give a very practical chemistry example, in which can be formulated as a system of first order differential equations. And the example I am going to take it is an example, similar to once that you seen in your chemical kinetics courses.

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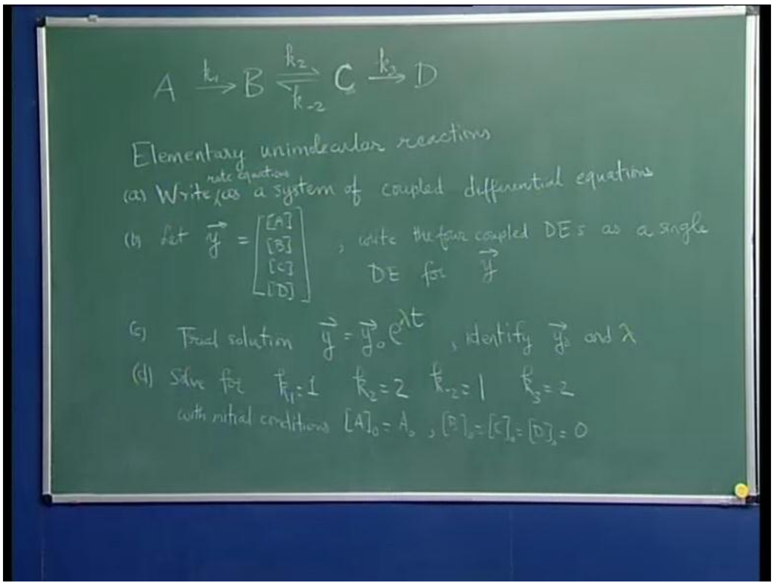

So, I will write the problem on this side and then we will write the solution on the other side. So, the problem statement is the following you have a series of reactions A going to B which reversibly goes to C and that gets converted to D. Now this is a set of elementary reactions and the rate of this reaction is k 1, this is k 2 the forward reaction, the backward reaction is k minus 2 and the forward reaction this is given by k 3. So, these are all elementary unimolecular reactions.

Now I will just go through the statement of the entire problem and then we will try to work out the solution. So, the first part is writing as a system of coupled differential equations and what I mean is you write the rate equations for all these reactions as a system of coupled differential equations. Second one so, we let y vector is a 4 component vector with 4 components A D.

So, it is a vector, it is a column vector the 4 elements of the column vector are the concentrations of A B C and D. So, let y equal to this and write the 4 coupled differential equations as a single differential equation for y, then the next part is you consider a trial function. So, trial function, trial solution y equal to y 0 e to the lambda t and identify y, y 0 and lambda. So, try the solution in the differential equation and you identify what y 0 and lambda related to, then d solve for k 1 equal to 1 k 2 equal to 2 k minus 2 equal to 1 and k 4 k 3 equal to 2. So, you solve this problem for this for these values of k with initial conditions A at 0 equal to A 0, concentration of B at 0 equal to concentration of C at times 0 equal to concentration of D at time 0 equal to 0.

So, initially the value of A is a 0 the value of B C and D are all 0, so you solved and solve using these values of k. So, this is what you want to solve and as we are solving this as problem you will see applications of the concepts of both linear algebra and first order differential equations. So, let us go ahead and work out each of the parts.

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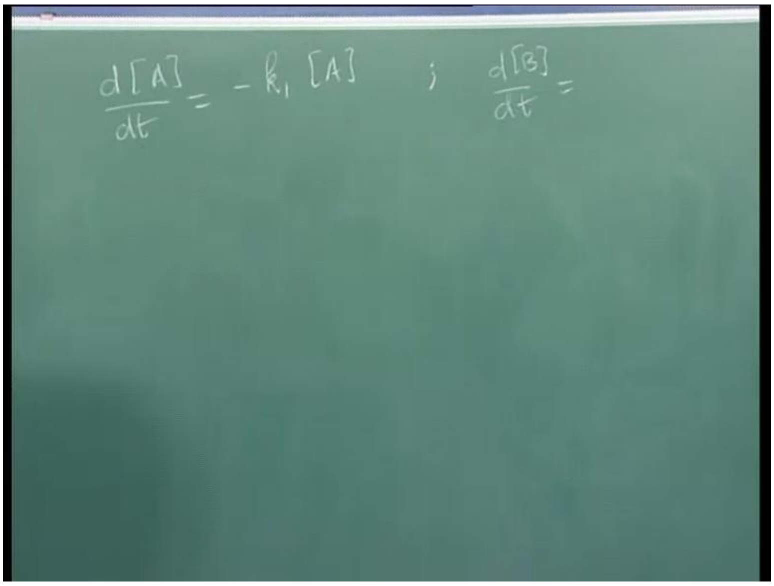

So, write the system as write the following rate equations as a system of coupled differential equation. So, I will just specify write rate equations so, let us go ahead and write that. Now the rate equations assuming all these are elementary unimolecular reactions. So, you can write D concentration of A by d t is equal to minus k 1 times A. So, the rate of this reaction is just k 1 times A.

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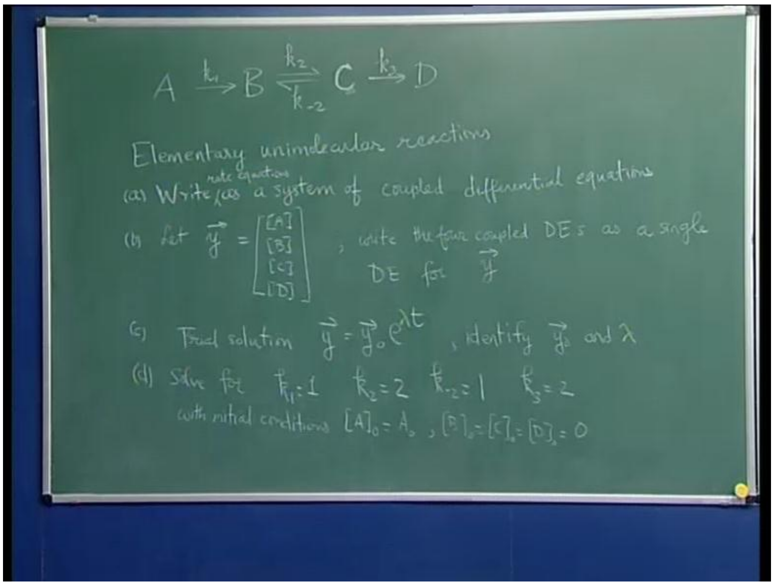

So, the rate of change of k with respective time is just minus k 1 A, then you can write d B d t, now the rate of change of B, B is produced due at a rate of k 1 A, B is produced at A rate of minus k 2, C when B is consumed at A rate of k 2 B.

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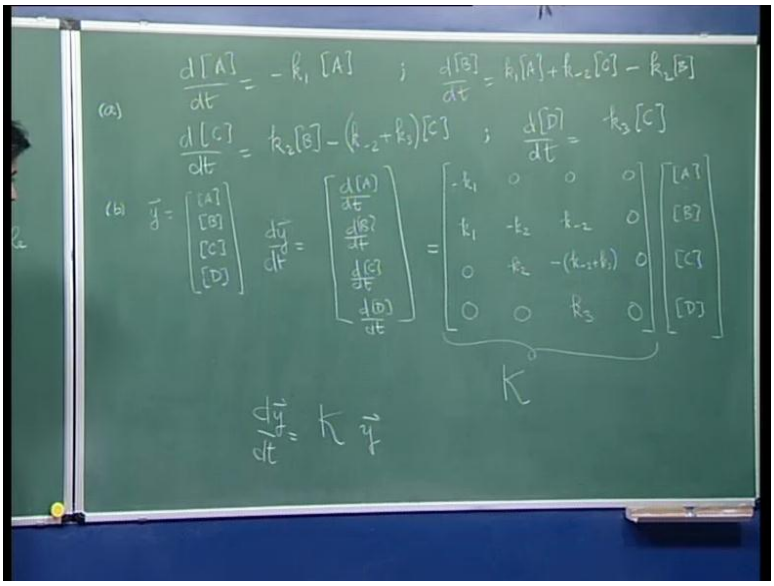

So, you can write this as k 1 a plus k minus 2 C minus k 1 B, then you can write d C by d t using similar arguments C is a produced in at a rate of k 2 B, but it is consumed at A rate of minus k 2 C and k 3 C. So, I can write k 2 B. This is the rate of production and it is consumed at a rate of k minus 2 plus k 3 C, will finally, D is equal to k 3 C. So, we wrote these as a system of coupled differential equations. So, we have 4 quantities A B C and D. The concentrations of A B C and D and each of them are changing with time.

And the differential equations for the rate of change of each of them is a they are all couple differential equations. So, the rate of change of B, depends on A C the rate of change of C, depends on A D and so on; and C depends on B and D depends on C. So, there is some amount of coupling between these various equations.

So, this completes part a, Now the b part, now here we say y is equal to A B D. Now we can write expressions we can write this as d y by d t is equal to d A by d t, d B. So, it looks very much like y but instead of A we have d A by d t instead of B we have d B by d t C we have d C by d t and instead of D. we have d D by d t. So, this is the vector corresponding to d y by d t. And now we can use the because d A by d t is given by k 1 A d B by d t is given by k 1 A plus k minus 2 C minus k 2 B. So, you can write this whole thing in the following form, so you can write this as minus k 1 0 0 0 times A.

So, now you can say that d A by d t will be minus so, when I multiplied this matrix to this vector the I will get a vector the first row of the vector will be minus k 1 times A and minus k 1 times A is d A by d t and that is exactly this equation. Then d B by d t I can write using the same argument I can say it should be k 1 minus k 2 and k minus 2 0 then this. So, that will ensure that d B by d t is k 1 times A minus k 2 times B plus k minus 2 times C. So, k 1 times A minus k 2 no minus k 2 times B plus k minus 2 times C. Now d C by d t I can write as…

So, you have k 2 times B. So, there is a k 2 here and you have minus k minus 2 plus k 3 C and then its independent of D and for D these two are 0 and this is k 3 that is 0. So, then I can write if I call this matrix as capital K. Then I can write d y by d t K y because this is simply y vector. So, d y by d t is a matrix K times y where, K is this matrix so. So, this completes part b of the problem. So, we are completed first we wrote it as a system of differential equations. So, remember that the concentration of A B C and D. They all change with time.

So, we wrote rate equations for how they change with time. And then after that we wrote this 4 coupled differential equations first order differential equations as one equation for a vector one vector for the rate of change of a vector and since it is a first order differential equation. This involves a matrix K. Now next in part c we want to use a trial solution, y equal to y 0 e to the lambda t.

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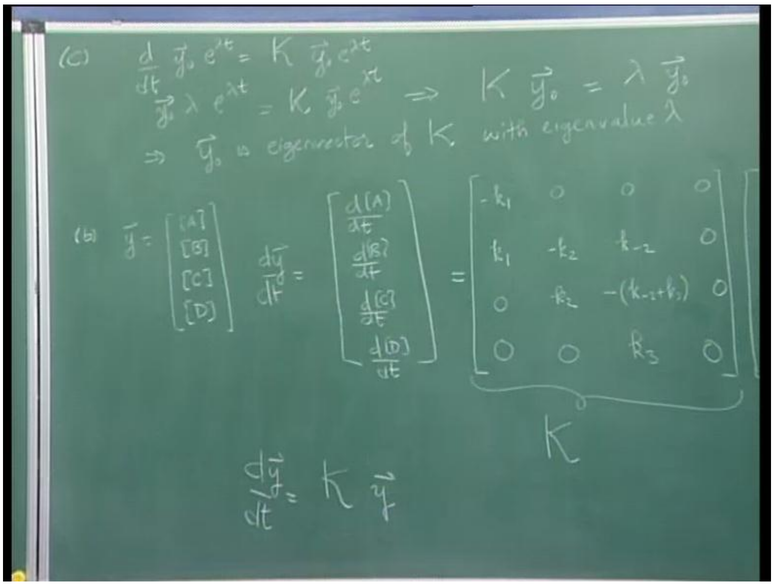

So, what we are going to do is we are going to substitute in this, we are going to substitute for y. And we are going to see what we get, so I will be keep erasing the top section and leave the bottom section. So, for parts let us go and do parts c of this problem. So, part c what we do is in this equation we substitute y equal to y 0 e raise to K t so, if I substitute that then I get d by d t of y 0 e raise to lambda t is equal to K y 0 e raise to lambda t.

So, all I did was wherever I had y I replaced it by y 0 e raise to lambda t. Now remember y 0 is a vector, but it is independent of time, so it can go outside this equation, so then what you left with is d by d t of e raise to lambda t. So, this will just give me y 0 lambda e raise to lambda t. So, I just take a derivative of this quantity, I just get lambda e raise to lambda t and this is y 0 vector and here I will get K, I just get y 0 e raise to lambda t. Now e raise to lambda t is just a scalar. So, I can cancel it from both sides and so, I get the equation so, this implies K times y 0, K is a matrix multiplying a vector y 0 is equal to and I just write this in the other way lambda is a scalar times y 0.

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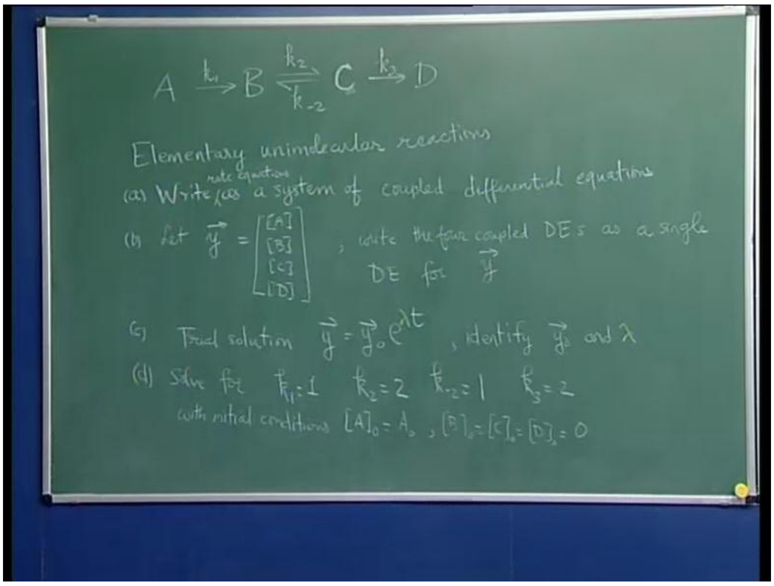

And this has exactly the form of an Eigen value equation, so this looks just like an Eigen value equation. So, this implies y 0 is Eigen vector of K with Eigen value lambda.

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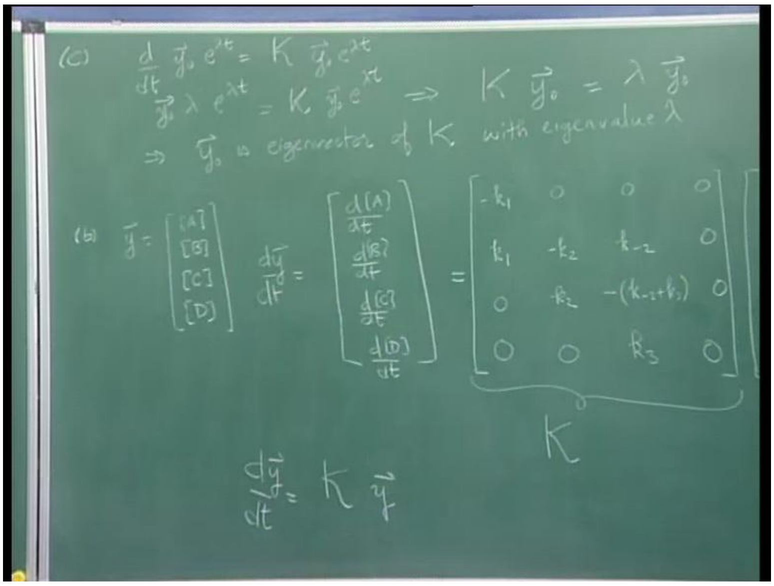

So, what we have done by this method is that we have shown that if we write the differential equation in this form, then our matrix K all we need to do, is to find the Eigen values and Eigen vectors of K. And then we have the solution to the differential equation. So, our problem of solving a set of couple differential equations is now reduced to a to finding the Eigen values and Eigen vectors of this matrix K. So, we can gone from problem of couple differential equations to an Eigen values and Eigen vector problem.

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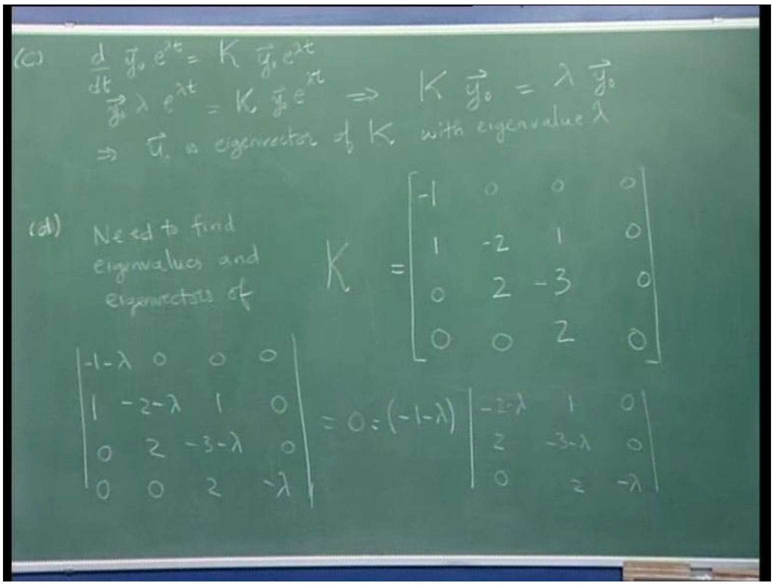

So, the next step will be to find the Eigen values and Eigen vectors of this matrix and that is what we do in part d. So, in part d we want to find the Eigen values and Eigen vectors of this matrix but what we are going to do is, we are going to substitute the values of values for each of these coefficients. So, when we substitute that I will just go ahead and fill it in here. So, you will get minus 1, so this is K equal to minus 1. k 1 is 1, k 2 is 2, k of minus 2 is 1, k 2 is 2, k of minus 2 is 1 and k 3 is 2, so 1 plus 2 equal to 3, so we get minus 3 and k 3 is 2.

So, this is my K matrix and according to this prescription, I need to find the Eigen values and Eigen vectors of this matrix. So, if I find the Eigen values and Eigen vectors of this matrix, then I can go ahead and find the general solution to this differential equation, to this set of couple differential equations. So, let us go ahead and try to find the Eigen values and Eigen vectors, in order to find the Eigen values of this matrix K. So, we need to find this is part d, we need to find Eigen values and Eigen vectors of K. So, we need to find Eigen values and Eigen vectors of this matrix. Now let us go and try to find out the Eigen values and Eigen vectors, so to find out the Eigen values what we do is along the diagonal elements.

We subtract lambda along the diagonals and we set the determinant of that matrix to 0. So, what will do is minus 1 minus lambda 0 0 0, 1 minus 2 minus lambda 1 0, 0 2 lambda 0, 0 0 2 minus lambda. So, we take this matrix we take this determinant and we set it to 0, and this determinant is relatively easy to evaluate, you can go ahead and try to evaluate it first of all we notice that this is the this 1 minus lambda factors out. So, this means this equal to minus 1 minus lambda times this smaller determinant that is minus 2 minus lambda 1 0, 2 minus 3 minus lambda 0 and 0 2 minus lambda. So, that is the value of the determinant and we can set it to 0, so if you go ahead and work out all the details we will get the following solution.

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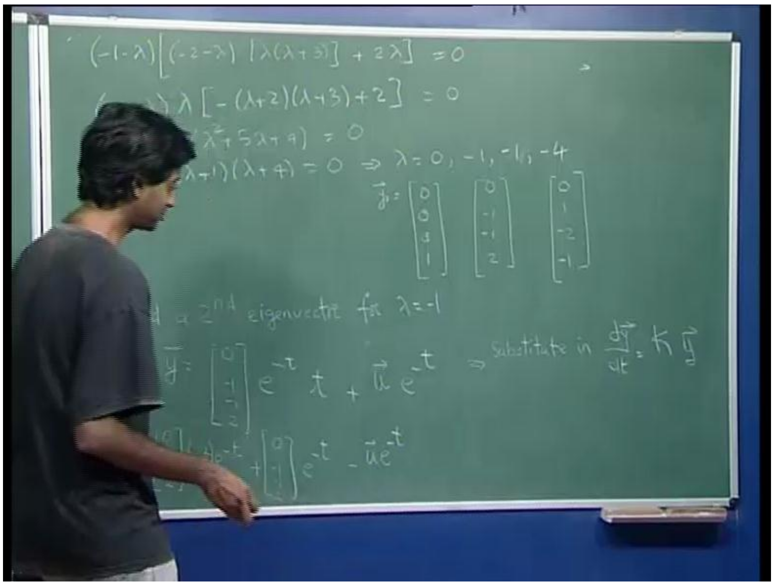

So, when we set this to 0 what we will get is minus 1 minus lambda times minus 2 minus lambda times the product of these two. So, I can write this as lambda plus 3 so that is the only term this term is 0 and then you have 1 and 2 this term is 0 so plus 2 lambda. So, you expand this out and this whole thing has to be equal to 0 so I can write this as minus 1 minus lambda and then and then I notice that I can take a lambda outside. So, lambda I can take a lambda common factor outside and then what I am left is minus of lambda plus 2 lambda plus 3 plus 2 and equal to 0.

So, I can write this as lambda I can always change this into plus, because multiplying by minus 1 there will be still give me 0. And then what I have is lambda square plus 5 lambda plus 6 minus 2. So, what I have is lambda square 0 and again I took a minus sign inside. So, you can think as so I took this minus inside. So, I have lambda square plus 5 lambda plus 6 and then I have a minus sign here. So, that is plus 4 and if you work this out you will get lambda plus 4 equal to 0.

So, this implies lambda equal to 0 minus 1 or minus 4 and this is a doubly degenerate Eigen values. So, I can write this as minus 1 minus 4 so, these are the. So, in general since we had a 4 since we had a 4 by 4 matrix we should have 4 Eigen values and 4 Eigen vectors but now we find that 2 of the Eigen values are identical. And we need to find the Eigen vectors next you can go ahead and you can actually evaluate each of the 4 Eigen vectors. So, I will just go ahead and give you the 4 Eigen vectors for lambda equal to 0 here y 0 Eigen vector y 0 is given by 0 0 0 1. So, corresponding to this Eigen value this is the Eigen vector corresponding to this Eigen value corresponding to minus 4 the Eigen vector is 0 1 minus 2 1 minus 2 minus 1.

Now, corresponding to 1 now corresponding to minus 1 this is a double degenerate Eigen value one of the Eigen vectors we can generate. So, one of the Eigen vectors is 0 minus 1 minus 1 2. So, if you put this back in the Eigen value equation you will get this Eigen vector, now we need to generate a second Eigen vector that is independent of this Eigen vector. In order to do that in order to generate the second Eigen vector corresponding to lambda equal to minus 1, we will use a trial solution.

So, we need a second Eigen vector for lambda equal to minus 1 so, we need a second Eigen vector since this is a doubly degenerate Eigen value you need two linearly independent Eigen vectors and to generate that we say we use the concept from differential equations and we say that we use y is equal to we take exactly this so, 0 minus 1 minus 1 2 e to the minus 1 t. So, minus t into t plus a constant vector that is u vector into e to the minus t. So, I will just try to explain this so, this part is the is y 0 e to the minus lambda is minus 1 t.

So, this is a solution to the differential equation, now we want a second independent solution. And so, what we will do is we will take the solution multiplied by t plus a constant. So, it is like when you had a when you have one solution and you want to find a second linearly independent solution, then you multiplied by x. So, it is in a very similar way we will use this as a trial second solution, now the only unknown here is u so we need to determine u. So, in order to determine u, we substitute this in d y by d t equal to K t.

So, substitute, this is a trial try y equal to this and substitute in K y. So, that was our original differential equation now when you substitute this in that. You will get one term due to the derivative of this.

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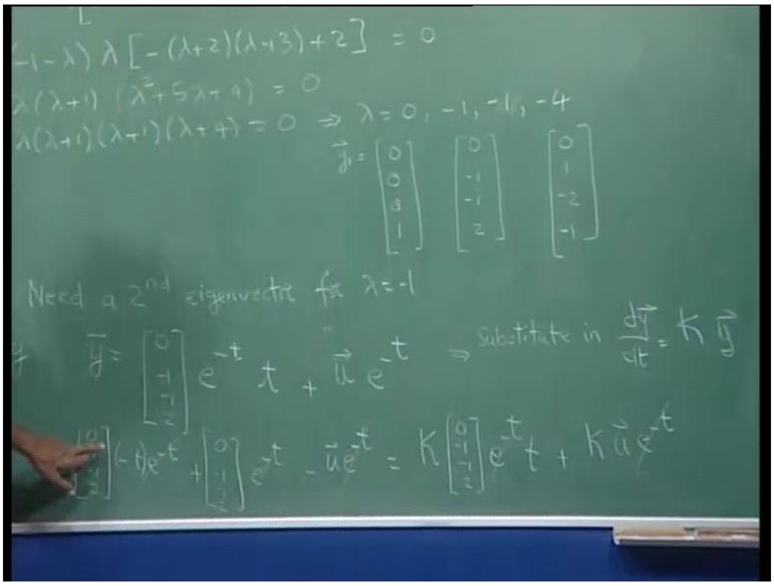

So, I will just write it out so, if I substitute this. So, first I am taking d y by d t. This is a constant. So, I will get then I am taking time derivative of quantities. So, I will have two terms so, the first term is minus t e to the minus t and the second term is second term is e to the minus t when you take a derivative of this. So, this is d by d t of this term now when I take d by d t of this term, I will just get minus u minus t. And on the so this gives me the left hand side in this differential equation d y by d t, now for the right hand side I get K.

Now the first term first term is just K 0 e to the minus t into t and second term second term is just plus K u e to the minus t. Now I can cancel each of the e to the minus t is everywhere. So, I can cancel this and also I notice that this is K times the Eigen vector multiplied by t and this is lambda that is minus 1 multiplied by the Eigen vector into t.

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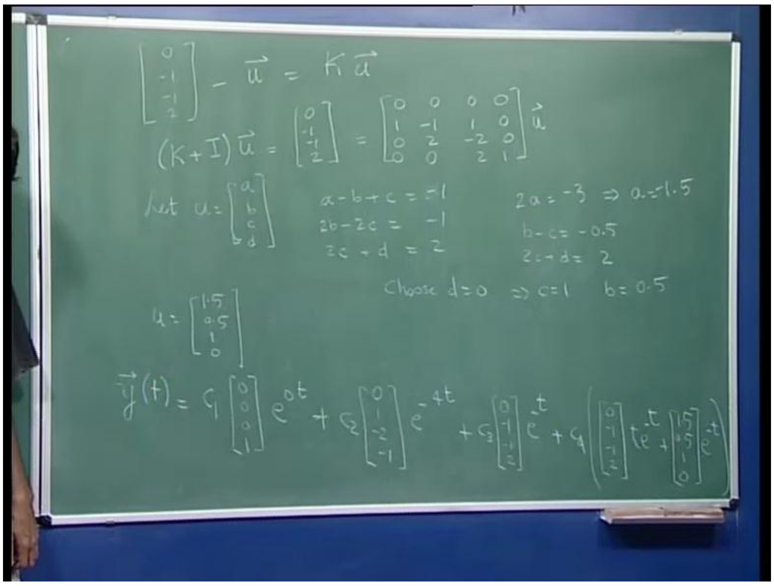

So, these two terms will cancel because this 0 minus 1 minus 1 2 is an Eigen vector of K with Eigen value minus 1. So, because of that these two terms will cancel. So, when you cancel the terms what you will get is the following expression 0 minus 1 minus1 2, minus u is equal to K times u. So, I cancelled all the e to the minus t and all the other terms and. So, what I get is exactly this in other words. So, I can write this as I can take the u to the right I can write K plus identity into u is equal to 0 minus 1 minus1 2 and since you already know the value of K. You can write this as this as so, if I do K plus identity remember K had a then I will get 0 0 0 0, 1 minus 1 1 0, 0 2 minus 2 0, 0 0 2 1 so this into u so the left hand side.

So, when I take K plus identity I will get exactly this matrix. So, this multiplied by u will give me this matrix and you can solve this for u. So, actually the first equation is satisfied for all values of u. So, you cannot determine all the coefficients uniquely because this matrix has the first row as 0. So, the rank is less than 4. So, you cannot be determining uniquely. So, let us say that we choose and in turns out that we can choose one of these arbitrarily. So, let us say suppose u is equal to a b c d, then I can say that I can write this equations as the first equation is just 0 equal to 0.

So, that is not really relevant the second equation I can write as a minus b plus c equal to 0 or equal to minus 1 the third equation I can write as 2 b minus 2 c is equal to minus 1.

And the last equation I can write as 2 c plus b equal to now this is b minus c a plus b minus c so, I can combine these two to give if I multiply this by 2 and added to this what I will get is 2 a equal to minus 3 implies a is equal to 1.5 minus 1.5 and then; obviously, this I can write as b minus c equal to 0.5 or minus 0.5. Now we have two equations b minus c is equal to minus 0.5 and 2 c plus d equal to 2. So, we have two equations and we have three unknowns we have already determined a and so these two equations and three unknowns cannot be solved cannot be solved for a unique solution.

So, in order to solve them we can assume one value for any of these variables and we will just choose a convenient value, we will choose d equal to 0. So, if I choose d equal to 0, we can see whether we can solve these two equations, this implies c equal to 1, b is equal to 0.5. So, then our u becomes 1.5, 0.5 1 0 so that is my u. Now I can write my general solution so y of t is equal to so now I had 4 Eigen values two of them where the same.

And I generated Eigen vectors corresponding to these, so then I can write my general solution in the following form, I can write it as a linear combination of each of these Eigen value equation each of these Eigen vectors multiplied by the corresponding Eigen value. So, I can write c 1 times so the Eigen value corresponding to Eigen vector 0 e to the 0 t so lambda equal to 0 was an Eigen value and the corresponding Eigen vector was 0 0 0 1. So, I multiplied by an arbitrary constant and write it this way then I take another arbitrary constant, and do the same for the next Eigen value.

So, the second Eigen value was e to the minus 4 t. So, lambda equal to minus 4, the corresponding Eigen vector was 0 1 minus 2 minus 1, the third and fourth where corresponding to lambda equal to minus 1. So, lambda equal to minus 1 had a one solution which had an Eigen vector 0 minus 1 minus 1 2 e to the minus t. And the last one c 4 now and now what we did to solve this we assume the form of y into t e to the we assume this Eigen vector into e to the minus t into t plus u e to the minus t.

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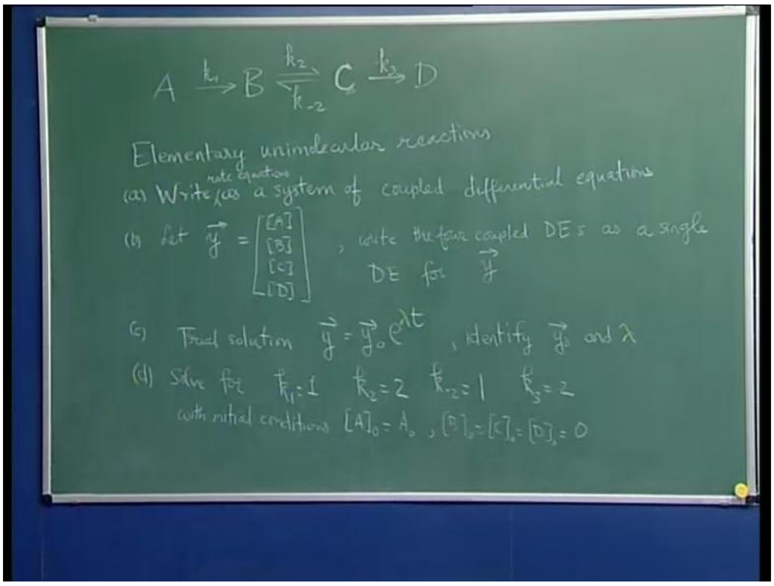

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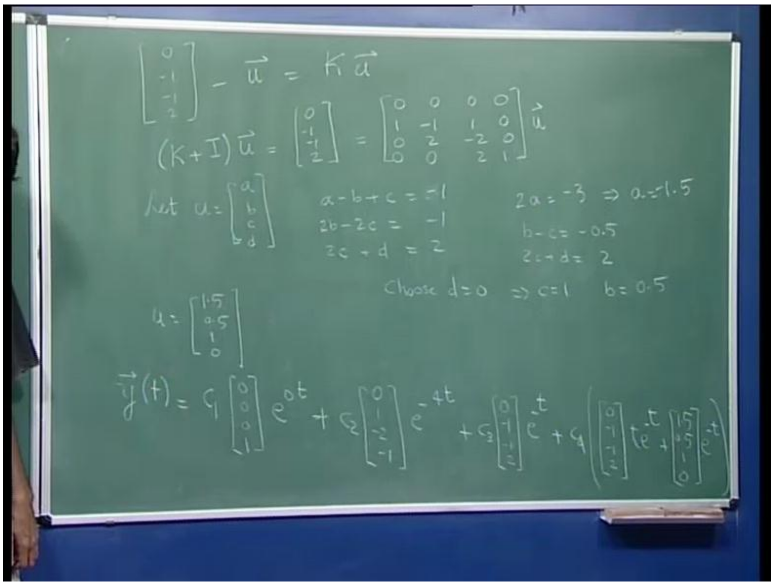

So, if we put all that together we will get 0 minus 1 minus 1 2 into t e to the minus t plus 1.5 0.5 1 0, that is our u e to the minus t. So, this is a general solution, now there were four first order differential equations so, we had a system of four coupled first order differential equation. Now so, there are four undetermined constants of integration but this is a most general solution of those four coupled first order differential equation for these values of K.

Now, in order to determine these four constants of integration what we will need to do use other boundary conditions or the initial conditions in this case. So, this is a general solution and now what we want to do is to find out the values of c 1, c 2, c 3 and c 4 using the initial conditions. So, let us go ahead and do that I will do it. So, we will try to put the initial conditions now according to the initial conditions a initial concentration of a is some constant initial concentration of b c and d are 0.

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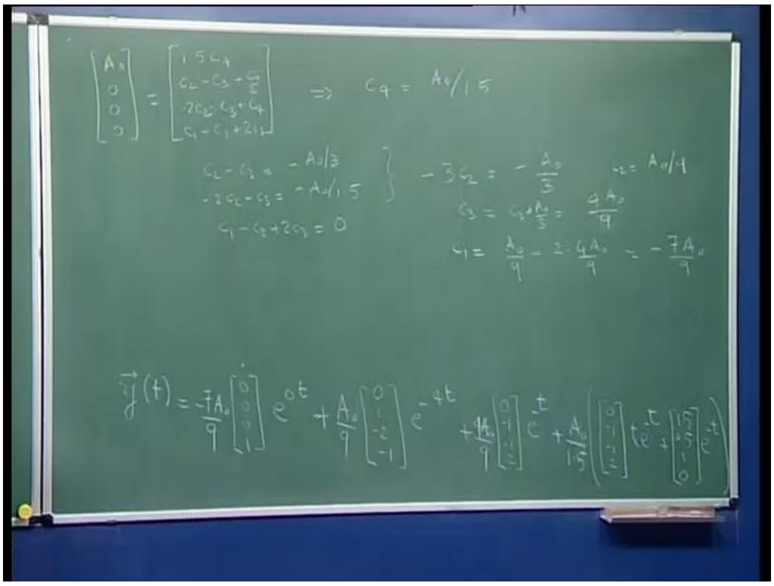

So, if I put t equal to 0 I mean t equal to 0, this term drops out entirely so, when t equal to 0, this will become 1, this is 1 and this is 1 this term drops out. So, when I substitute t equal to 0, I will get A 0 0 0 0 is equal to now c 1 times 0 so the first term has c 1 times 0 c 2 times 0 c 3 times 0 and c 4 times 1.5. So I get 1.5 c 4 and then I will get when I substitute here what I will get is c 1 times 0, c 2 times 1, c 2 times 1, minus c 3 so, c 2 minus c 3 so, what I will get here is I want some more space so the second term I will get 0 from here c 2 times 1 and since we put t equal to 0 this term gives me 1. So, c 2 times 1 and here I will get c 3 times minus 1 here I will get c 4 times, now this term will go to 0 because when t equal to 0 this whole term goes to 0 so, c 4 times 0.5. So, what I will get is c 2 minus c 3 plus c 4 by 2, c 4 into 0.5.

The next term so I will get c 1 times 0, c 2 times minus 2 so, minus 2, c 2, c 3 times minus 1. So, minus c 3 and I have c 4 times 1 plus c 4 and the last term will give me c 1, c 1 minus c 2 plus 2 c 3. So, c 1 c 2 plus 2 c 3 so this implies c 4 equal to A 0 divided by

1.5 so c 4 is determined uniquely. Now what about c 1, c 2 and c 3 so, in order to determine c 1, c 2 and c 3 we need to substitute in here so if we put c 4 equal to A 0 by 1.5. So, this is A 0 by 3, so we will get c 2 minus c 3 is equal to minus A 0 by 3. And then if I do this here minus 2 c 2 minus c 3 is equal to minus A 0 by 1.5 and last one will give me c 1 minus c 2 plus 2 c 3 equal to 0.

And now we can solve these again so, if we just take these two you can just subtract this from this. So, what you will get is 3 c 2 is equal to minus A 0 by 3 or you get c 2 equal to A 0 by 9 so c 2 equal to A 0 by 9 so, let us check again, so minus 2 c 2 minus c 3. So, this is minus A 0 by 1.5 plus A 0 by 3 that is minus A 0 by 3 and now you can calculate what c 3 is equal to 4 A 0 by 3 sorry 4 A 0 by 9. So, we have c 4, we have c 2, we have c 3, and now we can substitute here and we can calculate c 1 so c 1 is equal to so, c 1 minus c 2 plus 2 c 3. So, c 1 minus yes c 1 is A 0 by 9 minus 2 4 A 0 by 9 so, A 0 by 9 minus 8 A 0 by 9 so, that gives me minus by 9.

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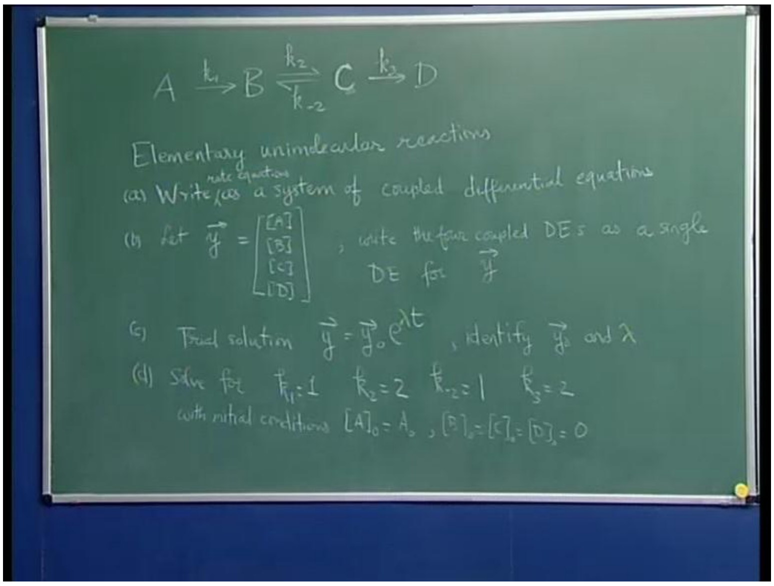

Now, we have determined c 1, c 2, c 3, and c 4. Now we have the general solution. So, the general solution, we can write down now in the following form so c 4 was A 0 by 1.5 c 3 was 4 A 0 by 9 c 2 was A 0 by 9 and c 1 was minus 7 A 0 by 9. So, this is a solution of this system of differential equations that satisfies these initial conditions. So, we have gone so, in this problem we have gone from this coupled kinetic equations. And we wrote it in the form of a matrix equation an equation for a vector, then we use this trial solution because we could write it as a d by d t of y as equal to a matrix times y; therefore, we could write trial solution of this form.

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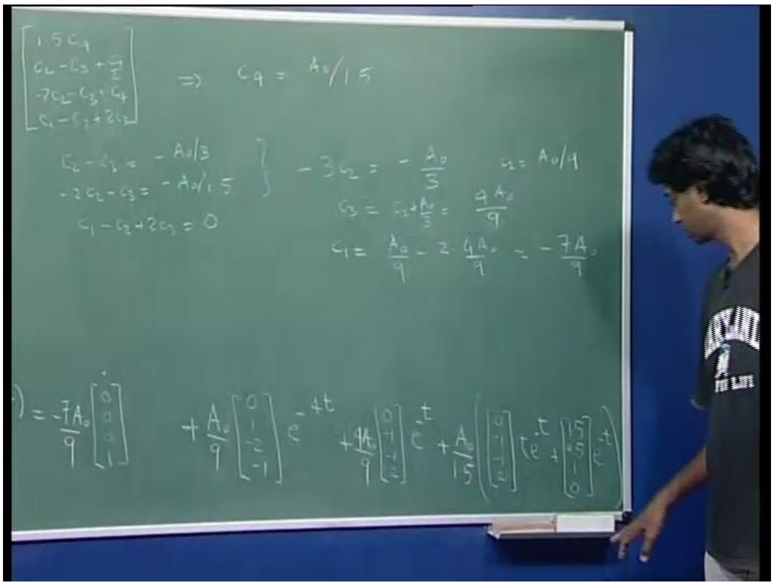

And you can go ahead and you can solve this equation what we notice is that when we substitute this into our differential equation. Then what we find out is that we need to calculate Eigen values and Eigen vectors of a matrix K. And we went ahead and we did that and after applying the initial conditions, we got this as the general solution. Now notice that this tells you how the concentrations of A B C and D all of them change with time. And I do not need to write this e to the 0 t because e to the 0 t is 1. So, using this method we can go ahead and we can solve any system of first order differential equations.

So, in the next class what we will do is we will go beyond first order differential equations. We will look at second order differential equations and there are a whole range of problems that involves second order differential equation. We look at the general solution, we look at the particular solutions and we will again go through the same exercise of different ways of solving second order differential equation.