Advanced Chemical Thermodynamics & Kinetics
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Lecture - 21
Advanced Topic in Chemical Kinetics - 3

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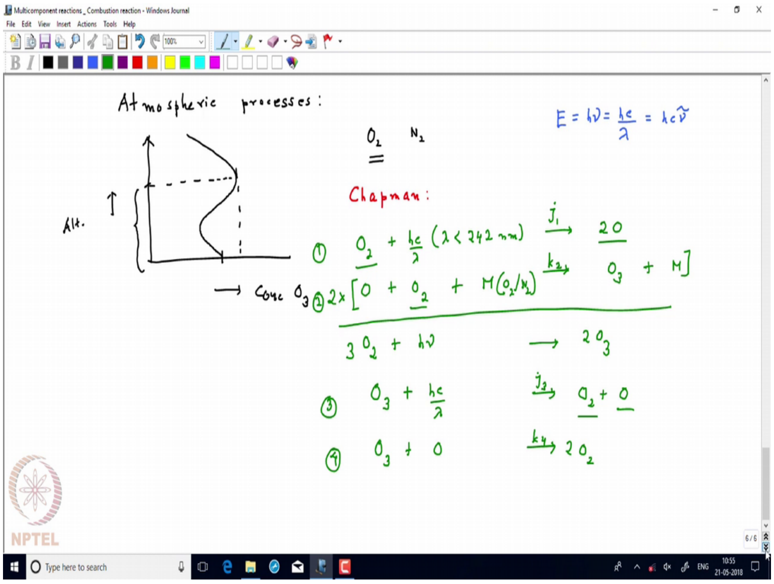

Atmospheric processes :

$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$

$\underline{\underline{O_2}}$ N_2

Chapman :

$$① \quad O_2 + \frac{hc}{\lambda} (\lambda < 242 \text{ nm}) \xrightarrow{j_1} 2O$$

$$② \quad 2\times[O + O_2 + M(O_2/N_2) \xrightarrow{k_2} O_3 + M]$$

$$3O_2 + h\nu \longrightarrow 2O_3$$

$$③ \quad O_3 + \frac{hc}{\lambda} \xrightarrow{j_3} O_2 + O$$

$$④ \quad O_3 + O \xrightarrow{k_4} 2O_2$$

So, we started our discussion on multi component reactions. And there we first covered the combustion process of combustion of hydrogen and oxygen to produce water. And today we will be discussing about another type of multi component reaction which is the atmospheric chemistry. Now under atmospheric chemistry again we will be talking only one particular problem that is basically formation and destruction of ozone, and there are many atmospheric processes or atmospheric we are talking about atmospheric chemistry, which is again photochemistry, because it is all the initiated by the ultraviolet radiation that reaches the atmosphere upper atmosphere.

Now, ozone formation and destruction is a very, very crucial for our survival, because you know that ozone absorbs the harmful ultra violet light and for which we survive. Because if it reaches on earth we can have many deleterious effect on our body which would be which are extremely deleterious for us.

For example, it can cause to damage of DNA and that can cause light induced cancer so, mostly the skin cancer. Now the question is what are the formation and destruction processes of ozone in the atmosphere? Now ozone is encountered in every layer of atmosphere. You also encounter ozone in this region of the atmosphere which we live in the troposphere but then you see a steady decrease of ozone. And usually if I draw the curve qualitatively if I plot say the concentration of ozone, and versus the height from the sea level or the altitude.

So, then we will see it varies very interestingly like it goes like this. And what I point out I would like to point out here is that at 0 altitude or basically on earth surface we have some ozone, and then it decreases, and then again it cuts on increases and reaches a maxima. And this region all of you know at some altitude, let say which of 20 to 50 kilometer region. So, this is basically the height for this layer which is known as ozonosphere. You have learned this term in your geography course.

Now, there you have a very high concentration of ozone. Now the interesting thing is the abundant species in atmosphere are oxygen and nitrogen. And oxygen is a major source for ozone, as well as ozone also produces oxygen. But the total amount of ozone is very very less. And if you think that if I increase the altitude and the air pressure of course, reduces and if you had all the ozone and if you put it in all the ozone which is present on our atmosphere. Then if you compress it to 1 atmosphere pressure, you will find that all the ozone will basically cover on a few millimeters 2 or 3 millimeter height.

So, which means actually ozone the volume of ozone, the amount of ozone is very very less but that is extremely important. So, compared to oxygen and nitrogen ozone is actually a trace element; trace are not element trace molecule in atmosphere. And, but still its existence is very, very important for our survival. Now there are many models for formation and destruction of ozone.

So, one of the very well accepted mechanism it is not it is well accepted in the sense that it is a one of the preliminary well accepted mechanism, there are also other mechanisms, that we will not discuss about all those things, but we will discuss the most standard mechanism, which is known as the Chapman mechanism, which was provided by suggested by Chapman. And then the Chapman mechanism says that the oxygen in our upper atmosphere, that actually absorbs light. So, I write h nu as a energy of the photon that is being absorbed. And this h nu the or say we can write it as a photon.

So, we can we could also write it as h c by lambda the energy of a photon. Remember that energy of a photon is nothing but h nu, which you could write it as h c by lambda where c is the speed of light in vacuum or h c nu bar where nu bar is the wave number. So, this lambda is less than 242 nanometer and beyond below 242 nanometer photons are absorbed by the molecular oxygen in the upper atmosphere.

And that actually produces the oxygen radicals. And again this is a radical chemistry, just like we discussed about radical chemistry in the earlier course bromine and hydrogen reaction to form HBR. And also in this course are just in the previous section we talked about hydrogen radical and oxygen radical and there we emphasize that the hydrogen radical is the predominant species, which actually takes the reaction forward not the oxygen radical because that is O-O bond energy is much higher.

Now, this ozone sorry this oxygen radical in the next step actually reacts with another oxygen molecule and to form ozone. But now you see that if I have one oxygen radical and one oxygen molecule is just an ozone is just like an adder like it is forming a bond. But then if there is a bond formation some energy has to be released, and somebody has to take up that energy. So, we in the same token like we discussed earlier that we write something like M, where M is the third body that actually absorbs the energy. And that M is usually the oxygen present in the atmosphere or the nitrogen, because these are the predominant species.

Now as you can see the overall reaction if we want to balance is stoichiometrically. So, I have to multiply it by 2, because I have 2 oxygen atoms which was generated in the first step. And then I will have an overall mechanism for formation of ozone, and that is O 2 in the presence of light. It is nu and that actually forms 2 O 3 and here I have 2 O 2 here I have O 2 so, I will have 3 O 2.

So, this is the overall balanced chemical reaction. Now just like ozone is formed in the presence of less than 242 nanometer light the ozone also absorbs light. And then it can actually degrade photo chemically to form oxygen and molecular oxygen and oxygen radical. Now this is I do not have the wavelength here, but this is usually the wavelengths which are above this 240 nanometer. It is a longer you wavelength and where actually ozone absorbs, it will be around some 2 I mean it is more than 242 nanometer wavelength.

So, this is also a UV photon, but that is a longer wavelength UV photon. Now this mechanism the destruction mechanism as I have shown here so, this is not a very predominant mechanism, the reason is a moment you have the radical, the radical can also I mean collide with O 2 and form you give you back the ozone molecule. Now the predominant destruction mechanism is another way. So, this radical can also react with molecular the ozone which is present. This is not a photochemical reaction, this is just a collision reaction, and then you can actually form 2 O 2.

So now actually I can write the rate constant for all these processes. Now let us just write the rate constant for this as j 1. Now I am not using the k notation here because it is a photochemical reaction. And secondly, I will use the k notation for the collision induced reaction; like, this is the second reaction so, if I call this as the first reaction, this is the second reaction. And this was the third reaction which is also photochemical reaction, I will write it as a j 3 the rate constant. And the 4th one was basically again collision induced reaction.

So, I will write the rate constant as k 4. Now as before we are assuming that already we said that O 3 concentration, ozone concentration is much less. So, we can assume that the oxygen radical concentration that is forming the ozone is also less, and there in a dynamic equilibrium. In the sense that this oxygen concentration as well as the ozone concentration in the upper atmosphere will be I mean independent of time. Meaning, the ozone oxygen radical concentration as well as the ozone concentration are always in a steady state.

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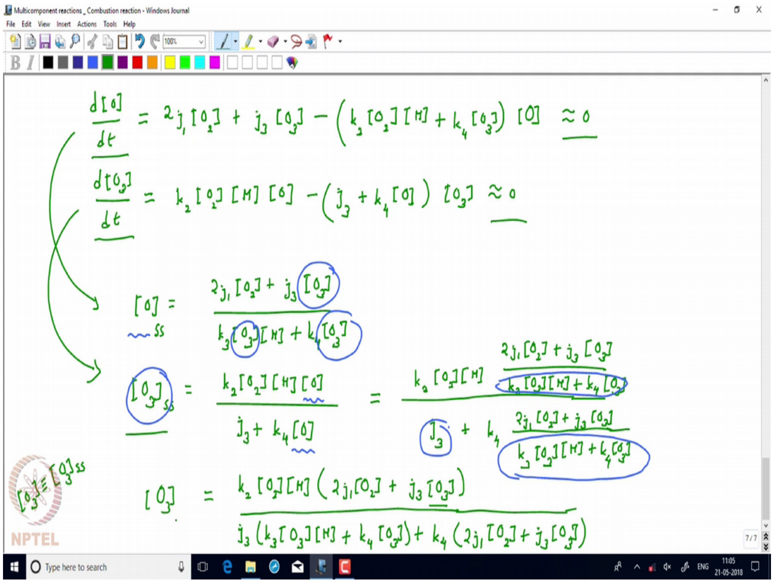

$$\frac{d[O]}{dt} = 2j_1[O_2] + j_3[O_3] - \left(k_2[O_2][M] + k_4[O_3]\right)[O] \quad \underline{\approx 0}$$

$$\frac{d[O_3]}{dt} = k_2[O_2][M][O] - \left(j_3 + k_4[O]\right)[O_3] \approx 0$$

$$[O]_{ss} = \frac{2j_1[O_2] + j_3[O_3]}{k_3[O_3][M] + k_4[O_3]}$$

$$[O_3]_{ss} = \frac{k_2[O_2][M][O]}{j_3 + k_4[O]} = \frac{k_2[O_2][M]\dfrac{2j_1[O_2] + j_3[O_3]}{k_2[O_2][M] + k_4[O_3]}}{j_3 + k_4\dfrac{2j_1[O_2] + j_3[O_3]}{k_2[O_2][M] + k_4[O_3]}}$$

$$[O_3] \equiv [O_3]_{ss}$$

$$[O_3] = \frac{k_2[O_2][M]\left(2j_1[O_2] + j_3[O_3]\right)}{j_3\left(k_3[O_3][M] + k_4[O_3]\right) + k_4\left(2j_1[O_2] + j_3[O_3]\right)}$$

So, if you assume those things so, calculation will be easier, and then so, first of all we have to find out what are the rates of oxygen radical formation, from this above equation. And that we will make it subsequently to be 0 so, that rate let us not put the 0 right now we will just see it afterwards. So, that rate if we follow the first equation you see, that 2 oxygen molecules are formed. So, for this rate again if I write the rate constant, stoichiometry will be here 2 of oxygen. So, I have to write the rate of formation of O as half d O dt. So, that half due to that half I have to multiply it by 2. So, I will have 2 j 1 into O 2.

Now, remember that when we are discussing the hydrogen oxygen reaction, there we took a rate constant, which is omega 0 which is here. So, there we have a slightly different notation, because we said that that this omega 0 is the rate it is not exactly rate constant it is the overall rate. And that is why if you remember that dh dt we are taking as omega 0, not as twice omega 0 into H 2. That omega 0 itself was a rate it was not a rate constant. And here we are talking about a rate constant which is the j.

So, we will use it as we use the other rate constant in chemical kinetics. So, it will be 2 times j 1 into oxygen molecule concentration. And then we have the second reaction as you can see here. In the second reaction actually oxygen radical that gets decomposed so, or we can actually first write the j 3 one where actually it is being formed. If you look at this j 3, it will be nothing but j 3 into O 3.

Now, let us consider the destruction path which is step 2 and step 4. Now step 2 it is basically O and O 2. So, we will have concentration of ozone times k 2 into concentration of oxygen times concentration of the third body into, I will have the concentration of oxygen radical. But that I am take common with the j 4 that is what I am just writing it outside. And plus for the 4th step I will have it will also be minus so, that is why I am taking it within the bracket. And I will have k 4 into O 3 into O, and that O I have taken common, and that I will eventually make to be 0.

So, I can write away solve for O, but before the under the steady state approximation. But before that let us also find out what is the O 3 concentration, how it is changing with time. Now if you go up O 3 is appearing here in the equation 2 may be you can use the same color here. And then O 3 is appearing here also and also equation 4.

So, let us just first write formation of O 3 O O from O and O 2. So, this will be nothing but k 2 times O 2 times M and times O. Then O 3 is being destructed into step 3 and 4. So, we will have minus j 3 into O 3 and it is k 4 into O 3 into O. So, we can actually write it in that way plus k 4 into O into O 3. That also we will keep eventually to be 0.

Now, then if we apply the steady state condition, from this first equation what we get is oxygen atom concentration. Now this is very straightforward as you can see. I will have 2 j 1 into O 2 plus j 3 in to O 3 minus not minus divided by because I will just divide by the entire thing which is in the parenthesis, I will have k 3 into O 3 into M plus k 4 into O 3. So, that is the steady state concentration of oxygen radical in the upper atmosphere. And similarly we can also figure out what is the steady state concentration of ozone in the upper atmosphere from this equation. And that will be nothing but k 2 this is also very straightforward O 2 into M into O divided by we will have j 3 plus k 4 into O.

So, then what we have to do? You have to see here that we have written the oxygen radical steady state concentration in terms of O 3. And similarly we have written the O 3 concentration in terms of the oxygen radicals concentration. So, basically these are 2 equations and for 2 unknowns. And we have to solve it and we can easily solve it. And if you solve it then you can actually get O 3 concentration. Basically we are what we are doing we are putting the value of the oxygen radical concentration here in this second equation. And then you will have a quadratic equation of course.

And then if you solve it I am not showing you the solution because it is very straightforward all wherever I have this O atom concentration. You have to write this entire term. And then that base I can show you one step, and then you can try solving it by yourself. So, it will be k 2 into O 2 into M times O. And instead of O I am writing 2 j 1 O 2 plus j 3 into O 3 divided by I have k 3 into O 3 into M plus k 4 into O 3. And in the denominator we have j 3 plus k 4 into O.

And again, we substitute for oxygen atom concentration 2 j 1 O 2 plus j 3 into O 3 divided by k 3 into 3 into M plus k 4 into O 3. And that now you can see that this part this entered part, that I can multiply it by j 3. And then eliminate that part from the numerator and the denominator. And then what we will get is something like k 2 I will have O 2 into M times will have 2 j 1 O 2 plus j 3 into O 3 divided by will have j 1 into the entire thing, sorry j 3 into the entire thing, j 3 into k 3 O 3 M plus k 4 O 3 plus have k 4 into twice j 1 O 2 plus j 3 in to O 3.

So, this entire equation you have to solve, and on the left hand side also I have O 3. This is steady state all the O 3 is actually O 3 steady state. So, do not get confused that this O 3 steady state is different than this O 3. So, this is just a notation because we have already approximated to be 0, and that is the steady state condition for both ozone as well as the oxygen. And then as you can see we will have a quadratic equation and then if you solve the quadratic equation.

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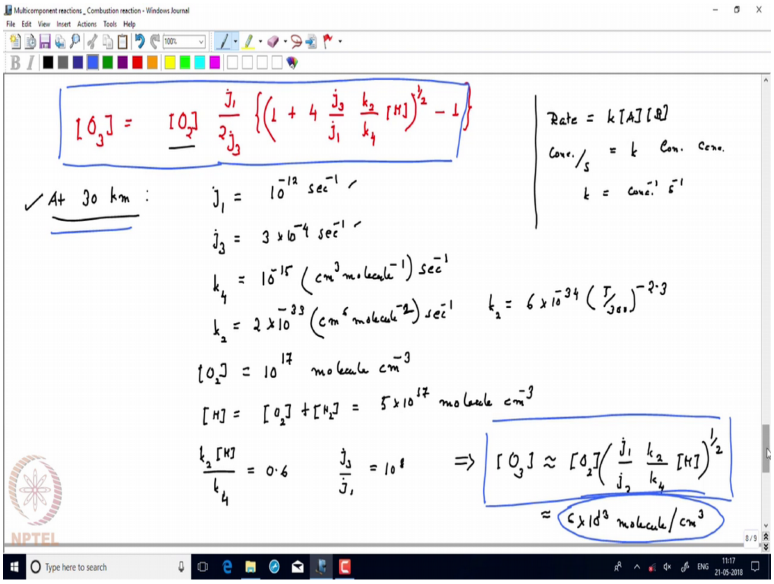

$$\boxed{[O_3] = \underline{[O_2]}\,\frac{j_1}{2j_3}\left\{\left(1 + 4\,\frac{j_3}{j_1}\,\frac{k_2}{k_4}\,[M]\right)^{1/2} - 1\right\}}$$

Rate = $k[A][B]$

Conc./s = k Con. Conc.

k = $\text{Conc.}^{-1}\ s^{-1}$

✓ At 30 km :

$j_1 = 10^{-12}\ sec^{-1}$ ✓

$j_3 = 3 \times 10^{-4}\ sec^{-1}$ ✓

$k_4 = 10^{-15}\ (cm^3\ molecule^{-1})\ sec^{-1}$

$k_2 = 2 \times 10^{-33}\ (cm^6\ molecule^{-2})\ sec^{-1}$ $\quad k_2 = 6 \times 10^{-34}\ (T/300)^{-2.3}$

$[O_2] = 10^{17}$ molecule cm^{-3}

$[M] = [O_2] + [N_2] = 5 \times 10^{17}$ molecule cm^{-3}

$$\frac{k_2[M]}{k_4} = 0.6 \qquad \frac{j_3}{j_1} = 10^{8} \qquad \Rightarrow \boxed{[O_3] \approx [O_2]\left(\frac{j_1}{j_3}\,\frac{k_2}{k_4}\,[M]\right)^{1/2}}$$

$\approx 6 \times 10^{13}$ molecule/cm^3

So, I have done on a few steps and you can solve it. And then what you will get is the final answer for the O 3 concentration, let me use a different color for this. So, the O 3 concentration will be in terms of oxygen concentration the molecular oxygen concentration O 2 into j 1 by 2 j 3 times we will have 1 plus 4 j 3 by j 1 into k 2 by k 4 times M. And this entire thing square root the square root is coming because it is a quadratic equation minus 1.

And now so, what you can see here this is a rather very complicated we make a complicated expression. Now we can actually estimate the magnitudes of O 3 which is the ozone concentration and O concentration. From we can; how do get it? You can actually get it from the data now how do you do this experiment? From upper atmosphere I you can do it in many different ways. For few atmospheric chemistry experiments, you want to simulate it in the lab, if you know the concentration and many other things.

But if you want to do a real experimental data so, what you do is a balloon experiment. So, basically you launch a balloon which will collect the composition of the gas from the upper atmosphere. And then you take it back and then you basically look at the kinetics there. And for kinetic measurement, you can you mostly use the absorption experiment based experiments.

There are also not spectrometric based experiments and then you combine all this data. And then you calculate what are the rate constants are, but you can also get an idea from the j of the j rate constant from measurement of photon flux in the upper atmosphere.

So, then for all these values let us say at we are saying at 30 kilometer, I have some data here which are real data collected by from experiments. So, j 1 now if you see what is j 1. j 1 is the this step, where actually oxygen gets dissociated into the radicals. So, that first order rate constant is 10 to the power minus 12. Second which means actually per second there are 10 to the power 12 times this thing is happening.

So, this is pretty fast decomposition. And j 3 is 3 into 10 to the power minus 4 per second the unit should be per second. What was j 3? If you remember, j 3 is this step where the ozone actually gets decomposed into O 2 and O and as I said that the O 2 and O because since O is very reactive can it again get back from your oxygen ozone molecule.

So, this rate is much smaller compared to your j 1. And then we also have the thermal rate for decomposition of a ozone is basically ozone and oxygen radical reaction to form you to form 2 oxygen molecular oxygen species. And that rate which is the k 4 that is something about 10 to the power minus 15. Now it is a bi molecular reaction if you remember.

So, it is an overall bi molecular reaction, this reaction as you can see. So, the rate constant will also be cannot be part second, because it is not a uni molecular decomposition. So, it will be 2 10 to the power minus 15 centimeter cube per molecule. So and usually are not using the mole per liter unit. So, here actually it is a molecule per cc unit. And that is a reciprocal of that concentration, and times second inverse. Because if you remember if we follow any second order rate equation so, the rate constant is something like k into the concentration of the species, let us say the species is A another species is B something like this.

Now, how do you write the rate? Rate is basically concentration, rate of change of concentration are second and then I have k, and then I have concentration and I have concentration here. So, the unit of k will be basically concentration inverse, second inverse for a second order reaction. So, this is exactly what we have done here.

So, just check the units and then for the 3 body recombination there are some tabulated function, in the sense that you can get it again from a huge after you collect huge data from your balloon experiment and many other experiments. And then there are some standard tabulated data. So, for k 2 now the k 2 was basically 3 body rate constant. And that we will write the equation will write units correctly, but before that we are just writing the table.

So, it basically from some very complicated power law with temperature. And at the temperature which is around say 30 kilometer altitude that k 2 if you calculate from all these parameters, you will get all the atmospheric parameters. You will get something a 2 into 10 to the power minus 33 centimeter to the power 6 per molecule, and then second inverse. This should be per 2 molecule because I am taking the square of that that is why it is coming centimeter to the power 6.

Now, then if all the also you what you need is the concentration profile of O 2, because as you can see the O 2 is here. And you need a concentration profile of O 2 at 30 kilometer altitude because as we said the majority of the ozone actually stays between 20 to 50 kilometer altitude. And then you can actually calculate the O 2, and this O 2 again these are just data which I am writing.

Just to give you a feeling, what will be the final result of these rates. And that O 2 concentration is found to be 10 to the power approximately 10 to the power this is also kind of all are actually approximates. So, you do not need to write it for oxygen molecule concentration explicitly, 10 to the power 17 molecules per centimeter cube. And then the total M which is basically the as I said that M is a third body, but the third body is the abundant species. And that abundant species are oxygen and nitrogen. And that if you calculate it will be 5 into 10 to the power 17 molecule per centimeter cube.

Now, why 5? Because as you know that we have 80 percent nitrogen and 20 percent oxygen so, if oxygen is 10 to the power 17 so, that forms actually one 5th of that. So, the total M or the third body will be 5 into 10 to the power 17. And then we can actually estimate this term which is k 2 into M divided by k 1. And that will give you something like k 2 into M divided by k 1. That will be 0.6 and j 3 by j 1 that will be around 10 to the power 8 and which now can lead to a more simplified expression.

So, as I can say see here. So, I have a k 2 here. And should have a k 1 it is it is not k 1 it should be k 4 k 2 by k 4 and then after you use all these parameters. So, that will give you the ozone concentration is approximately equal to the molecular oxygen concentration times j 1 by j 3 into k 2 by k 4.

Now, this into M to the power half and then you can actually evaluate the O 3 concentration for several species, and like if we know the values of put the values of j 1 j 3 as well as k 2 and k 4 and also at the estimated value of M. So, that will give you something around 6 into 10 to the power 13 molecules per centimeter cube. So, this is basically the final value for ozone which is around 30 kilometer. Now here as you can see going from here to here this expression, we made some approximations, because we said that what is the relative ratios of k 2 by k 4 into M and whatever the j 1 and j 3.

So, all these values we put and that is why you are getting this particular equation that we have shown here. Now if you move on, so, I will just leave it as an exercise how would you get this particular expression which I am putting it in the box, from this expression which we kind of showed we did not show the derivation, we showed only a part how to proceed. And then we said that you try to derive it. So, you try this derivation.

And once you get that expression. Try to figure out how this how this relation is coming under these approximations; are not approximation, under this experimental values. And then if you can use these experimental values to approximate.

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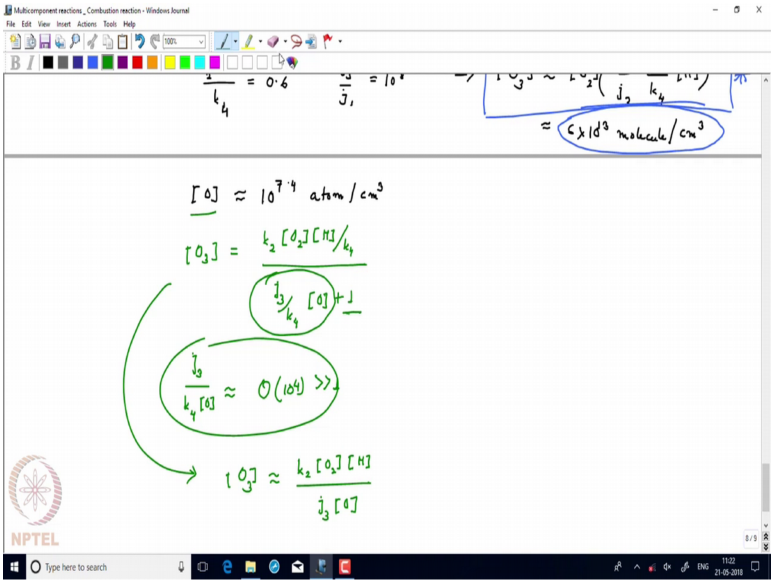

$$[O] \approx 10^{7.4}\ \text{atom/cm}^3$$

$$[O_3] = \frac{k_2[O_2][M]/k_4}{\frac{j_3}{k_4}[O] + 1}$$

$$\frac{j_3}{k_4[O]} \approx O(10^4) \gg 1$$

$$[O_3] \approx \frac{k_2[O_2][M]}{j_3[O]}$$

Approximation means actually you can neglect some of the ratios of the rate constant or some concentration, and how we can get this approximated value of ozone, at say an altitude of 30 kilometer. At a particular temperature which corresponds to that particular altitude.

Now, what is interesting is that you see in a similar way, you could also calculate the oxygen radical’s concentration. Because remember that we wrote the oxygen radical also in terms of O 3, and then we put that value in the equation of O 3. So, that you will get around after you put all these values, it will be something like 10 to the power 7.4. Now you have to be very careful, this is basically particles per cc, but I cannot write it as molecule per cc, that is basically those many atoms per cc.

So, molecule per cc means it is molecules per cc could write it we could write it as atoms per cc. Now if we now rearrange these equations which is the 3 expression, let us go back, where we got this value, see the expression of say O 3 that may actually use a different color. So, this expression so, I have k 2 into O 2 times M into O divided by j 3 plus k 4 into O. So, that equation if we rearrange little bit, then we will get k 2 into O 2 into M divided by k 4 the k 4 1 were just putting up and in the denominator I have j 3 divided by k 4 into O plus 1.

So, that is a very straightforward, we are just dividing the numerator and denominator by a k 4. And then since we know that this thing j 3; we already know that thing j 3 divided by k 4 into O. So, that will be on the order of let us say, it will be something like 10 to the power 4, how do you get it? You can easily get it from these values you have the j 3, you have k 4.

And you also calculated an approximate value for O this one and if you put back all these values which is much larger than 1. So, this is much larger than 1. So, I can actually neglect the one value here. And then this expression if I use this condition, this expression for O 3, now becomes something like k 2 into O 2 into M divided by j 3 into j 3 into O. So, we have j 3 here, or we could write it as the ratio of O 3 and O.

So, we have a 3 here, and we have oxygen atom in the denominator. J 3 k 4 into O, let us actually have a quick look. So, what we are writing here is j 3 into O. So, I have already ignored the one compared to that. So, you can actually ignore that. Yes, now you can actually from this; you can calculate the ratios of the ozone and O radical. And this is very important. Now why it is important? It is important, suppose if I just take that particular ratio O 3 and O.

Let me quickly also check the O 3 value here before we discuss it was k 4 into O as we can see here.

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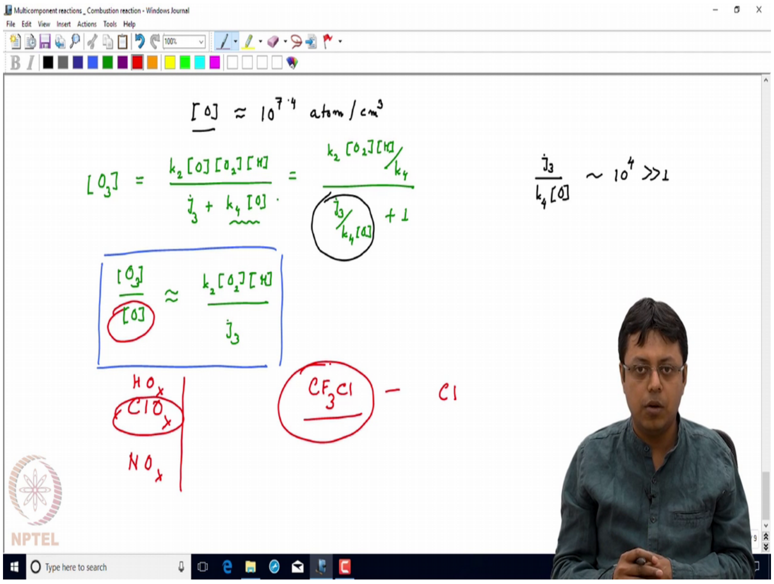

$$[O] \approx 10^{7.4} \text{ atom/cm}^3$$

$$[O_3] = \frac{k_2 [O][O_2][M]}{\dot{J}_3 + k_4 [O]} = \frac{k_2 [O_2][M]/k_4}{\dot{J}_3/k_4[O] + 1}$$

$$\frac{\dot{J}_3}{k_4 [O]} \sim 10^4 \gg 1$$

$$\boxed{\frac{[O_3]}{[O]} \approx \frac{k_2 [O_2][M]}{\dot{J}_3}}$$

HO_x

ClO_x

NO_x

CF_3Cl – Cl

So, now let us go back and see what was the value of O 3 which we got in terms of oxygen radical. We can actually rewrite this expression so, talking about this particular expression O 3 steady state, which is k 2 O 2 times M times O divided by j 3 plus k 4 into O. Let us just rewrite it here. So, O 3 concentration which we got earlier in terms of the O concentration of the oxygen radical concentration is k 2 times O times O 2 times M divided by we have j 3 plus k 4 into O.

Now, can actually divide the numerator and the denominator by k 4 into this term so, let us write it what will be the final expression. So, I am just rearranging the terms again. So, it will be k 2, O will cancel I will have O 2 into M divided by k 4. And then I will have j 3 divided by k 4 into O plus 1. So, that is just a rearrangement. Now the thing is this j 3 into k 4 into O, that value we can evaluate from all this parameters that we have written like j 3 here. We have k 4 here, and we have also estimated the O here. So, what we can write here like j 3 divided by k 4 into O. And that will come around 10 to the power 4 which is much larger than 1. So, this term is much larger than 1.

So, what we can say that this is approximately will be if I just ignore the 1. And again multiply the numerator and the denominator by say k 4 into O. Finally, what we will get is something like this. We will get O 3 divided by O will be equal to k 2 times O 2 times M divided by j 3. Now this is a very very important relationship. Because this is an overall equation where if we see the ratios of ozone molecule present in that higher altitude, divided by the oxygen radical concentration.

Now, this concentration as we can see that there kind of the ratios of the oared oxygen species which is present in the upper atmosphere. Now this if we can actually the reactions that destroys either oxygen or O 3, now that can result in a direct reduction of O 3. And in the removal I mean so, that way we can actually see this particular ratio actually is very, very important to know about how much the destruction process of the formation process is happening.

Because if we have more ozone coming then this ratio will be high but if we have the oxygen radical species which are more, then and have the decomposition of ozone also will take place because of the 4th reaction k 4. And we have already estimated or shown you some of the values of the rate constant. And that is a non-negligible value the k 4 values.

So, this ratio is very, very important whether I am actually enriching ozone or I am actually decreasing the O radical concentration. And since more or less all these values k 2 O 2 j M and j 3 are kind of constant. Then this is also a constant. So, that is why the ratio of the ozone and oxygen radical. That always is kept at constant. And although we said that individually also that they are constant, because all these things we derived remember, using the steady state approximation for both oxygen radical O radical as well as the O 3 the O zone.

So, individually they are constant as well as the ratio is constant. But this ratio actually fluctuates from one particular atmospheric region to the other atmospheric region. Now what I did not discuss in this particular formation or destruction of the ozone there are also other an atmospheric products, like say for example, chlorine cycle, and then you have chlorine actually forms many oxide compass which we call as C l O x where x can be 1 2 something like that.

Similarly, I also have nitrogen oxide cycles which are called as NO x cycles. So, these NO x cycles, clock cycles as well as the H O cycle, which is H O x cycle, which as a part of it we also talked about. Because we talked about H O H radical, chemistry a little bit, when you talked about H 2 and O 2 reaction but that is a combust process, that is basically manmade process. But it can also happen atmospherically. And all this that beauty of this and the complexity of all these processes is that, they are kind of couple because you have some common spaces. As I said that ozone cycling have the oxygen radical, that oxygen radical is not a part of a zone cycle it also is a part of the clock cycle, it is also part of the other cycles.

So, the problem here is that all these cycles are not independent of each other. The way the Chapman model actually approximated it is not fully correct because there is a very complex connection between this through this intermediate or the common species. Common radical species, it can be molecular species and for that all these cycles are interconnected. And that makes the atmospheric chemistry the study of the atmospheric chemistry which we have to study because of our own survival. And that makes the subject so interesting.

Because you have so many parameters and so many coupled differential equations. So, we will not actually talk about the details. But the final thing is that this use of this chlorofluorocarbons as you know that this kind of molecule CF 3s C l which is known as Freon. So, this was used for refrigeration as a coolant agent in refrigerator.

And then people found that this CF 3 cell gets into the atmosphere and that forms this chlorine radical. And that actually is an important constituent of the clock cycle that actually produces the oxygen radical. This species and that eventually can destroy the ozone all these reactions which you have discussed.

But again we have not discussed the full photochemistry of ozone. And people found that these are very, very harmful and that actually create ozone hole in and that leads to basically penetration of the harmful ultraviolet radiation through these ozone hole and to the earth surface, and that causes a skin cancer. And that is why chlorofluorocarbons are banned for to be used as refrigerant coolant. And so, 3 people actually brought enormous insight among many others into the mechanism of this formation and destruction of ozones. Mario Molina, Paul Crutzen and Cheryl Rowland and they were given the chemistry noble prize for their interesting work.

So, in the handout will mention this particular work by Melinda, Sherrod and Rowland which actually led to all these interesting discoveries and making a connection of the chlorofluorocarbon, how it influences or basically leads to the formation of the ozone hole which is very dangerous for us. So, we will stop our discussion on the multi component reaction here.

So, we talked about combustion chemistry, we talked about the ozone formation. So, in the problem set what we will be asking is that we will ask you to work out other I mean other problems like other cycles. For example, for combustion there are also, hydrocarbon combustion we can actually give a problem on this hydrocarbon combustion. And for example, for atmospheric chemistry, we can actually give a problem on this NO x cycle or clock cycle, and ask you to solve the differential equation.

Again these are all just simple mathematics. And you just have to choose and we will give you this information that which radical species you take to be under the steady state concentration. And you make that approximation and then you just solve the differential equation. And then we will also give you some values to make further approximation. And then at the end of the day it should be able to get a filling. So, what are the how this understanding of the mechanism can actually lead to an understanding of a very, very common phenomena like as I said that the formation of the ozone hole or something like that. So, stop our discussion here on the multi component reaction.

Thank you.