Environmental Air Pollution

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Lecture 8

Atmospheric Formation of Air Pollutants - 2

If you recall, we were doing something here last time. We modelled the things last time and we were kind of close to answering the questions: what the ozone levels could be? And why? And how?

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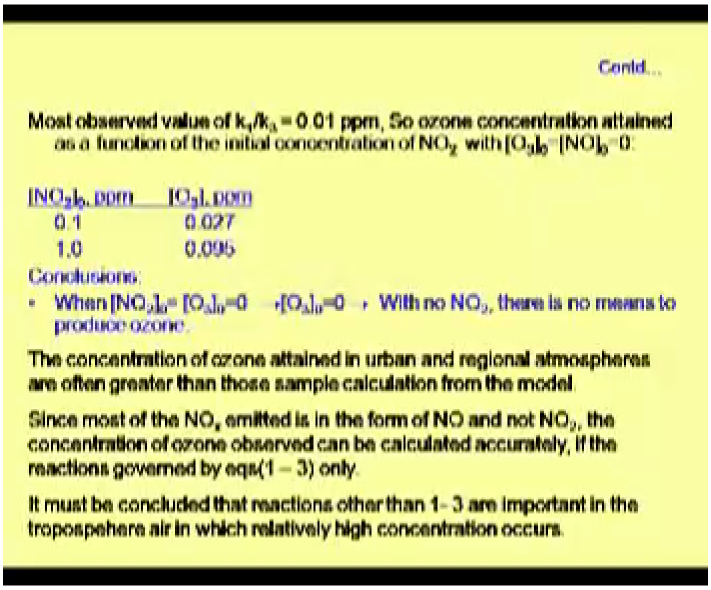

But when we came to the level that we went to the field and we were trying to say if really the atmosphere behaves the way we thought the model should; we concluded that the model really failed. The simple reason for this was: the ozone levels were much higher than what the model credited it to be. That is where I had left you to think as to where the problem was.

If you recall, what I said was that we cannot really look just at a little box, the way I was trying to model; the box should be a true atmosphere. We just cannot put NO in there, NO_2 in there and let the sunlight come through that one and hope that the ozone will be formed. Ozone is formed; no doubt about that, but we have to look at the atmosphere as I said which is a very complex thing; there are thousands of reactions occurring at one time, competing with each other, being decided as to who will be formed, who will be surging ahead, who will be falling behind and things like that.

What we will do in this class is go through some other reactions that might be occurring in the atmosphere and then try to answer, to some extent, that where and how ozone could be little bit larger. So that is where I want to go from last class and then we will go to lecture 8 and the slide show. We had seen the importance of the OH study.

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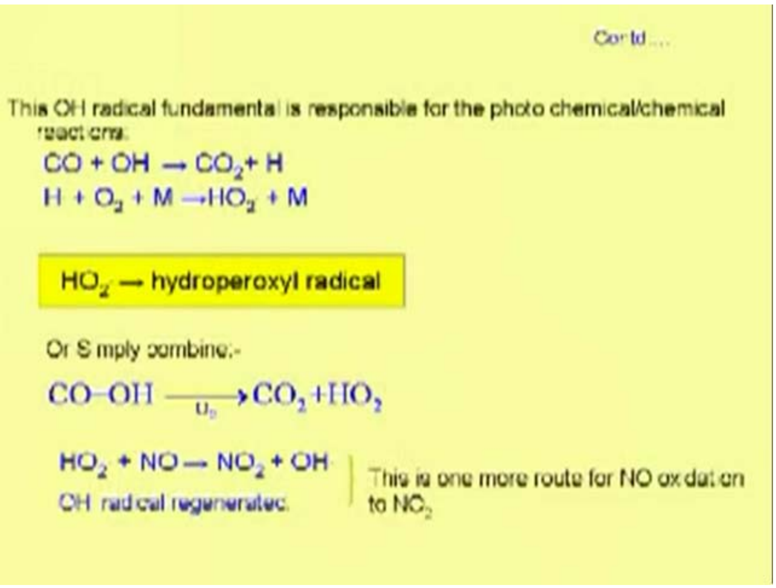

Simplest thing; Carbon monoxide will suddenly be in the atmosphere. So let us see apart from the OH radical that was formed, what it can do to the CO for that matter. CO is generally a very unreactive gas. We all know that. It does not even react with the moisture; it needs very high temperature for that. Even when are talking, when we inhale CO, CO does not react anywhere. CO goes all the way to the lungs and gets transferred into the bloodstream; we all know that. Whereas, for example, ozone is so highly reactive that it does not reach deep in our lungs; it reacts in [ ] only; whatever [fact] needs to do, it does it in the upper respiratory part, but here even CO is affected by the OH radicals. You see that it can form CO_2 and it can also give rise to atomic hydrogen. Atomic hydrogen can be very reactive and form HO_2.

I know we have heard about H_2O but in this course also you will alo understand what HO_2 is. HO_2 is a very fundamental, important radical in atmospheric chemistry. We will talk more about HO_2, but just think that HO_2 can be formed by OH, by a simple reaction. Can someone very quickly tell me how we formed the OH? Quickly tell me how was the OH formed? What are the routes for the OH formation? Because we did discuss yesterday that OH is formed.

Student: NO is reacting with water. [Conversation between student and Professor not audible (04:30 min)]

NO reacts with water? NO. Please tell me. Look into the things; you should take some broad notes at least and tell me why and where did the OH come from? Because you see we do not know.... [Conversation between student and Professor not audible (04:54 min)]

What was happening with ozone breaking down? Did we discuss ozone break down? It forms the nascent oxygen; the nascent oxygen can be in two forms: ground state and excited state; ground state can react with oxygen, can give me back ozone; if it is in excited state, it cannot react with oxygen. We said that or did we not say that? Did we say that or did we not say that? If we have not done that then I want to do it again, but if I have done that, then I don't want to do it again.

Tell me: do you recall what I am saying? Or you do not recall it? I think we did it. We did it, right? Or do you want me to do it again? We did; we did a lot; in fact, we did it in detail.

[Conversation between student and Professor not audible (05:48 min)]

Student: Sir you have given ozone fertilizes and ozone plus etcetera.

Ozone fertilizes and it can fertilizes depending on the UV radiation the photolysis of ozone is in two paths; the two path ways are there: in one way it can make the oxygen which is at the ground state and that ground state oxygen can react again with oxygen to give me back ozone. So, that is with more of null process; nothing has happened really. The other route is depending on the UV radiation wave length, it can produce atomic oxygen which is in the excited state; that cannot react with oxygen to produce and give me back the ozone. Rather, that O which was 1 D if you recall, we had mentioned it, that can react only with or that can react with many things, but it also likely to react with water. So O which is in excited state plus H_2O will give me what? Twice OH and that is where the fundamental thing that I got OH. So do not forget last class what we discussed.

The whole photochemistry revolves around OH radical and it is a very fundamental thing. So we had OH and then now the new thing, which we are talking, is the formation of the HO_2

radical - that is the hydroperoxyl radical. The interesting part is, you can summarise these two equations in simple form: C plus OH radical, plenty of oxygen, CO_2 and HO_2 and this HO_2 is capable, rather hugely capable, of oxidizing NO to NO_2.

Just see, there are some more things, other than the ozone, to oxide NO into NO_2. Last time, when I gave you the reaction we only said that the thing which can oxidise NO to NO_2 was ozone; you remember that? But there are the other rules also. Anyway, what I am saying is, we are starting with CO and then this the additional source through which I can produce NO_2. What is happening is that not only the ozone but I am able to put more NO_2 in the system. So partly it will also, if you have more NO_2, the only way the ozone in troposphere can be formed is by dissociation of NO_2. I repeated this again and again. If I have an excess of NO_2 obviously I had not considered CO in my earlier model, for example, so my model failed.

Looking here, what I am saying is, there is something more going on than the little box that we considered last time. There, in the box, we had only put NO, NO_2 and little initial ozone concentration, and then expected that we should get the things, but it did not happen the way it should have. You see there is already an additional pathway of forming the NO_2 just by considering little amount of CO, and then again everything is triggered by OH radical. Do not forget that an OH radical is critical. Now, you should also not forget where the OH radical come from. And then, the funny part is that we generated.... I have available for more are producing HO_2 and more of conversion because OH is back. Although OH is ao reactive, that the concentration in atmosphere is very small and I told you that the amount of the concentration was in some molecule like 10 to power 11 molecules per litre per meter cube.

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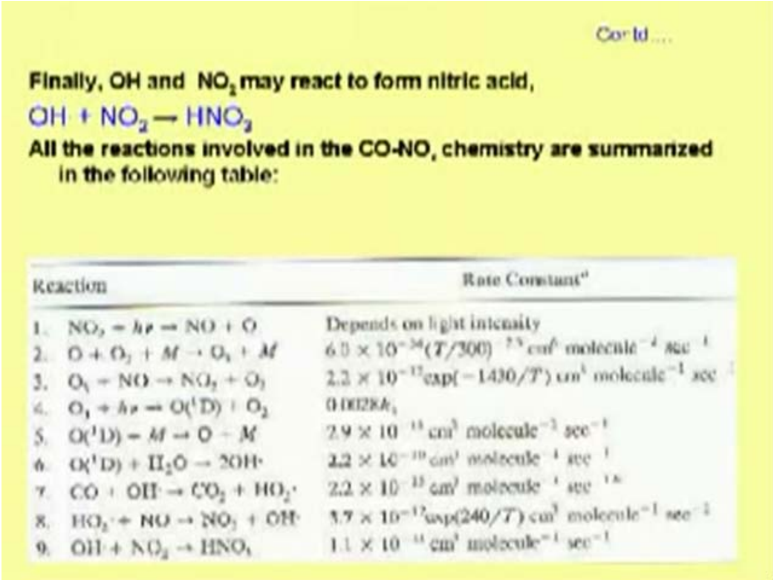

Reaction	Rate Constant[a]
1. $NO_2 + h\nu \rightarrow NO + O$	Depends on light intensity
2. $O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-34}(T/300)^{-2.3}$ cm^6 molecule^{-2} sec^{-1}
3. $O_3 + NO \rightarrow NO_2 + O_2$	$2.2 \times 10^{-12}\exp(-1430/T)$ cm^3 molecule^{-1} sec^{-1}
4. $O_3 + h\nu \rightarrow O(^1D) + O_2$	$0.0028k_1$
5. $O(^1D) + M \rightarrow O + M$	2.9×10^{-11} cm^3 molecule^{-1} sec^{-1}
6. $O(^1D) + H_2O \rightarrow 2OH\cdot$	2.2×10^{-10} cm^3 molecule^{-1} sec^{-1}
7. $CO + OH\cdot \rightarrow CO_2 + HO_2\cdot$	2.2×10^{-13} cm^3 molecule^{-1} sec^{-1} [b]
8. $HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$	$3.7 \times 10^{-12}\exp(240/T)$ cm^3 molecule^{-1} sec^{-1}
9. $OH\cdot + NO_2 \rightarrow HNO_3$	1.1×10^{-11} cm^3 molecule^{-1} sec^{-1}

We also said that if you have plenty of NO_2 being formed much faster than it can be consumed by ozone, there is a terminal reaction that the NO_2 comes out of the system. There has to be a sink for everything. So what we are saying here is that you had the excess of NO_2 and you also had the OH radical, it can convert to HNO_3 and this is one of the routes for forming the acid and removal of NO_2 from system because this reaction cannot go back. There is also a removal mechanism for NO_2 from the atmosphere.

This is a little summary of the things of reactions we have done so far. You recall this equation; you recall this; you recall this (Refer Slide Time: 11:08 min); you recall the excited state giving you the O - that O can react with water and form the two OH radicals. That is what just now I said, now this OH radical, now there are the additional things; OH radical can convert CO_2 and form the HO_2, HO_2 – what was it? Hydroperoxyl radical. Then this HO_2 is able to oxidise NO and just not the ozone. This can also oxidize to produce NO_2. OH is regenerated and there is also reasonably good possibility, that if you have more NO_2 then it can be consumed by the ozone. Then you have the OH radical and it can go into the terminal stage and get out of the process. The NO_2 gets out of the process and forms HNO_3. What happens to HNO_3? We will see it a later, but they are the rate constants and the way we write the equations, we can also write the model for this. This gives the summary of what we did. Let us recap.

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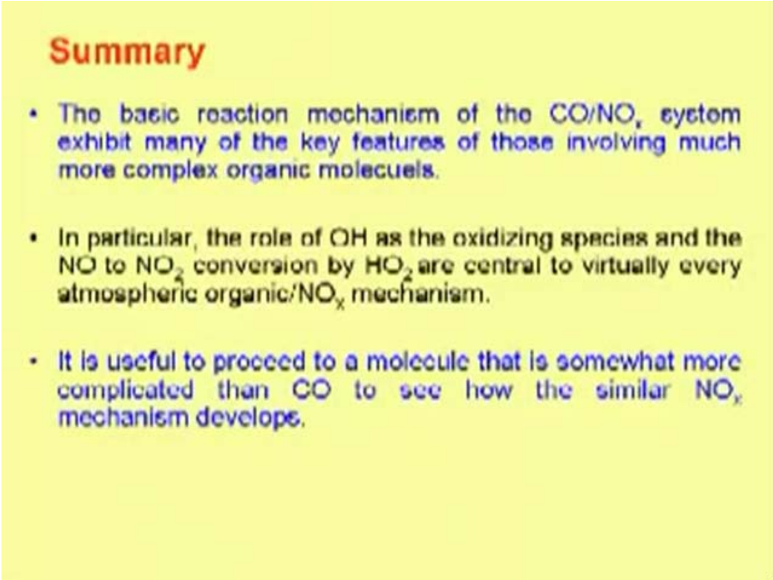

The basic reaction mechanism for the CO/NO system exhibits many of the key features of those involving much more complex organic molecules. We just consider a very simple thing, in particular the role of OH as the oxidizing species and the NO to NO_2 conversion by HO_2 are central to virtually every atmospheric organic NO_X mechanism. I gave you one example and will give you more examples; there are many more ways through which you generate HO_2. If you are able to generate HO_2 it means you are able to oxidise NO much faster to NO_2. If NO_2 is formed, you are forming ozone all the time. So see how there is a little turn around in our model. Then we can say well how more ozone should be formed in the atmosphere, just not by the simple models. It is useful to proceed to a molecule that is somewhat more complicated than CO and let us see what happens.

This is another example of the atmospheric chemistry, coming up with the formaldehyde. Formaldehyde is a very important pollutant. It is directly emitted from automobiles and from the combustion processes, largely from petrol driven vehicles. We will see why HCHO comes from petrol driven vehicles. This HCHO again is pretty reactive.

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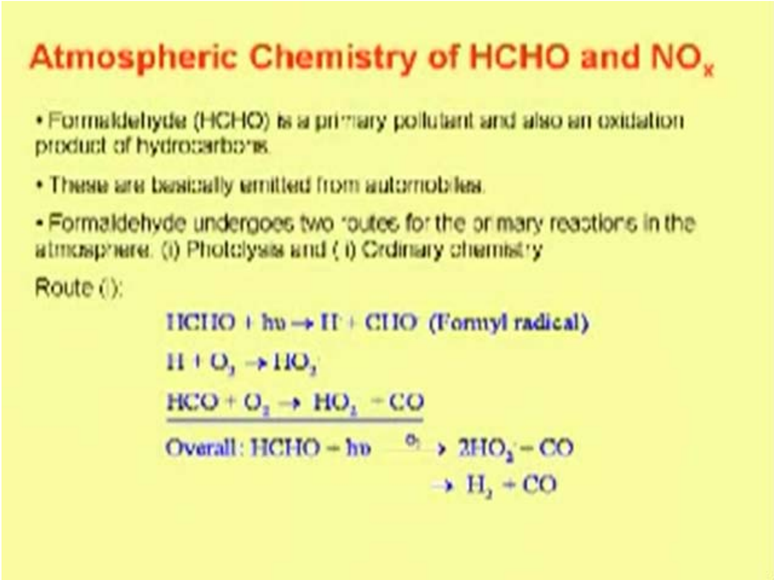

The formaldehyde, HCHO, is a primary pollutant and also to some extent the secondary pollutant formed in the atmosphere. These are basically emitted from the automobiles and formaldehyde undergoes two routes. For the primary reaction in the atmosphere, one is photolysis and another is ordinary chemistry. Let us see the two routes HCHO. Again the H_{mu} that we are getting onto the earth, the one wave length, which is reaching on the earth, can break it down to the atomic hydrogen and then formyl radical and this atomic hydrogen can react with the oxygen present to give the HO_2. More HO_2.

Then this HCHO can also combine with the oxygen to give you more HO_2. Another reaction which can happen is this route. It can go out of the system also by hydrogen combining with the hydrogen to produce the hydrogen. This, you see here, this can go this way or this can go this way. This is the summary of this, but this is the ordinary reaction that we are talking about. It can also form the hydrogen and CO and the things are happening competitively. It is not that well this is happening, this is not happening and that is decided by what? Which will happen faster? Which will happen slower?

[Conversation between Student and Professor - Not audible ((00:15:34))]

Also the rate constant and things like that; that particularly governs, you know dc by dt, it depends on the initial concentration and the rate constant: how quickly things will change? Who will become first? Who will be more? Who will be less? You should not forget the importance of the rate constant.

These are the two routes. Again we took the example of CO, we get another example of HCO and again what we get is the HO_2. Once we are getting HO_2, you are again forming the HO_2. What is this route two business? If you really see it is an [overall]; that is what we are getting. What are we getting [overall]? Is that what we are getting? Go back to the previous reactions. In route two it can also form the HO_2, CO and H_2 O.

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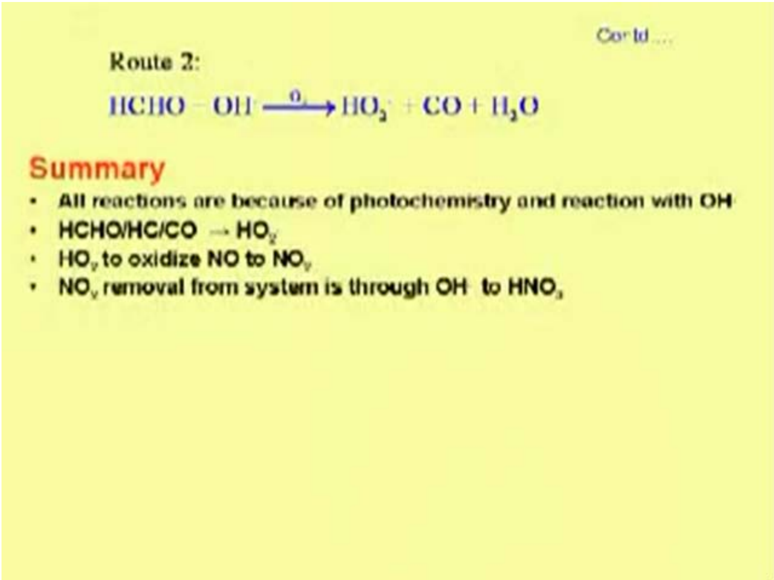

In summary what do you want to say: all reactions are because of photochemistry and reaction with OH radical; HCHO, HCCO and it will give to HO_2. What does HC mean here? Hydrocarbons.

In general, broadly speaking, the hydrocarbons will also give you the HO_2 and if we have the HO_2, it will form NO_2 and NO_X removal from system that can also happen. We should adhere the NO_2 can also give rise to ozone. The only route of forming the ozone in the atmosphere or in the troposphere is by the breaking down of NO_2.

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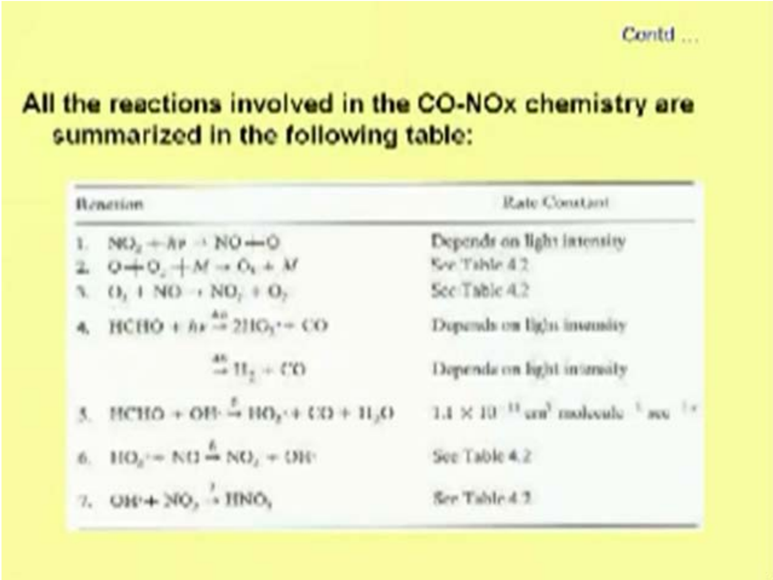

Let us summarise these reactions: All the reactions involved in CO, NO_X chemistry are summarised here and that is the repetition. This HCHO, if you remember it was formed the HO_2 and then it can also terminate in the form of the hydrogen and carbon monoxide. This is another reaction: HO_2 plus NO will give you NO_2, regenerates OH radical and this is the terminal reaction. Writing the same thing what we have discussed, but in addition to writing this, we are also writing its constant. This, when I am referring to table 4.2, please see Sheffield. You really need to look at that because these things were given in the first lectures, but this thing is more less can, and again remember, the units of the K can be very different.

Now let us model the whole thing, as we did last time. Do you remember the model that we prepared was this one: K_1 upon K_3, NO_2 upon NO that we have done in the last class. If I have to write the steady state equation for this system for - CON/COH reaction and also involving HCHO. So, what you see here at a steady state, of course do not forget that.

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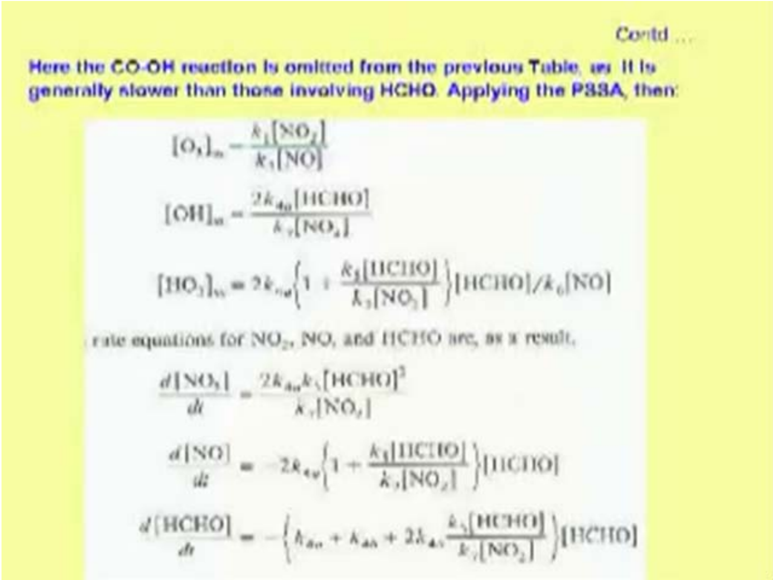

You have to write the reaction for dc by dt equal to zero and through some algebra. You will find the OH steady state concentration will remain on the reaction 4 and reaction 7. That is how you will derive it. This you can derive it; it is more or less of algebra; at steady state, do not forget that. Then you can find out what will be the steady state concentration of HO_2. In the atmosphere that will involve the rate constant or certain reactions and involve the HCHO and require the NO and that sort of thing.

We can also write our equation in terms of variability as a function of how the d NO_2 .... Now, do not forget that now the d NO_2 should involve the HCHO and this is how the NO will change, how the HCHO will change. Mostly this is the algebra that you need.

You are little familiar with this one; in the next class I will give you one assignment, that will involve this thing because seeing is one thing and doing is another thing. If you do the run through that assignment, you are able to analyse it. Now, if you see, if you are able to write it... What we are now trying to do now is this.

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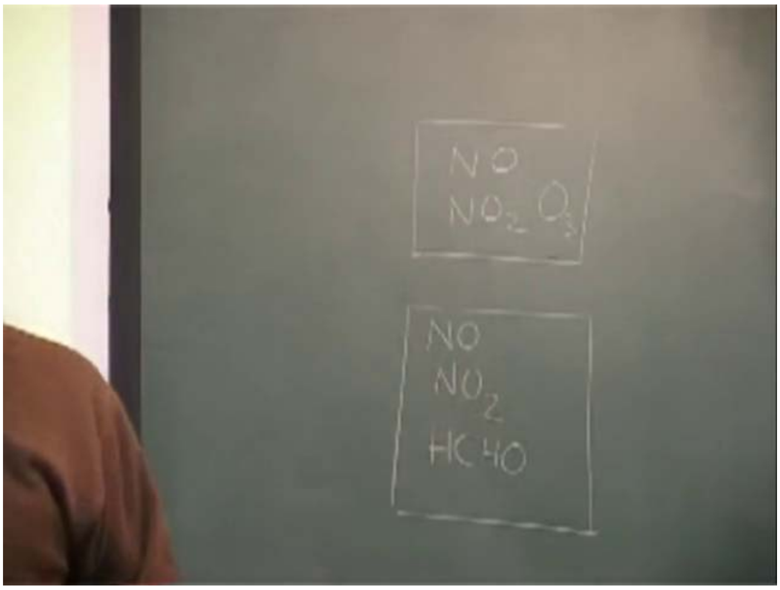

The first thing we did yesterday is we took the box and something like ozone. We are making it a little complicated; we are having the box and I have modelled it here. The results of this model, we should try to understand.

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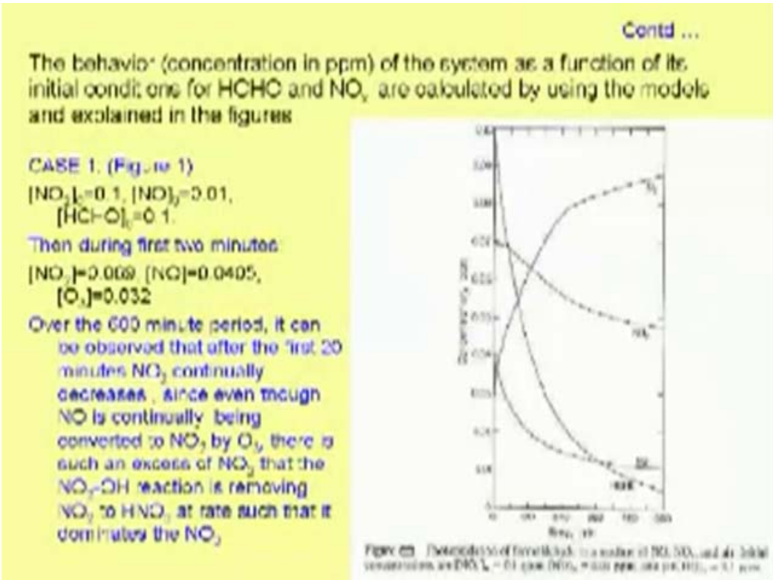

I will explain what the things are but first of all, see if it took the initial concentration NO_2 as 0.1, NO as 0.01, very small quantity comparatively, HCHO is 0.1. Let us take this example and then we solve the things. What happens is before HCHO can do something, the first reaction that we are talking about of this kind, they react, resettle quickly, their equilibrium settles quickly. When this is settling quickly in a moment, what is happening to NO here? It is converted to NO_2. So what will happen? Where is NO? You see an NO?

[Conversation between Student and Professor - Not audible ((00:22:26))]

This is NO, you see here NO; what is happening to NO? We had the NO_2 and then the NO. What happens is that NO_2 and the NO increases a little; why? Because you see here the ozone is formed quickly. First of all, immediately what happens is that NO_2 is attacked and it quickly reduces. The first thing will happen will be to NO_2; because, we have NO_2 in the system. We have started, NO was less, how much was the NO_2 and how much is the NO. NO_2? NO_2 is much higher - 0.1 and this is NO is 0.01. Please pay attention; this will require some attention.

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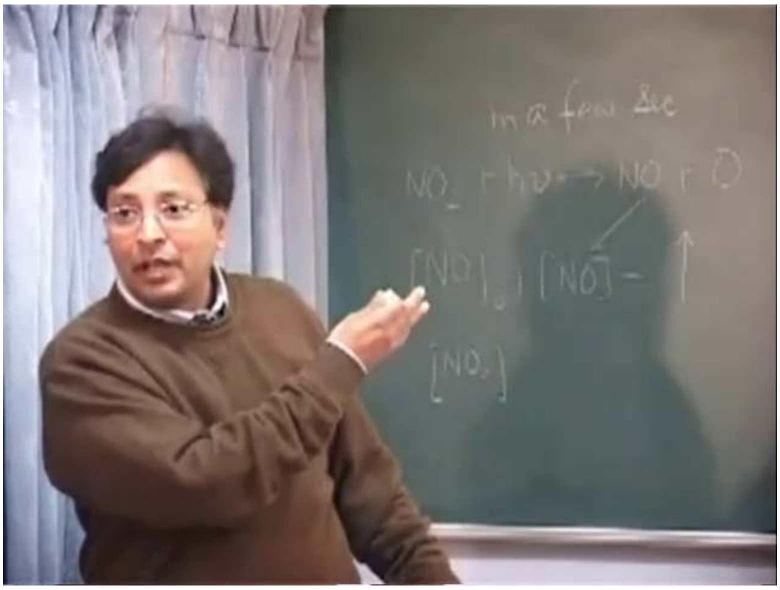

I have lots of excess of NO_2 what will happen is quickly, within seconds, NO plus O. So I already had some NO, 0 plus this NO; what will happen instantly? NO level will rise. You started NO with 0.01 and within seconds it went to 0.045. It takes of from here and shoots to 0.45. We have the reason that is why it should be, so it goes up, all happening in few seconds. You will see that ozone is formed then you will see that that ozone also picking up from 0, quickly going to some other level within a very short time and it will change rapidly.

What will happen once I have gone high on NO and I also am going high on ozone now? What will happen to NO? It should go down eventually, peaks immediately and then NO goes up. What will happen to NO_2? It should ho down, eventually. Peaks and immediately goes down. What will happen to NO_2? Why should it decrease? How can both decrease? How can both NO and NO_2 be decreasing? Look at the picture. Are they both decreasing? Ozone is going up, that is fine. More and more ozone is formed. Any clue? Can you find clue from here?

Convert into HO_3. All things happening now. Now, what you are getting is: you are forming more and more NO_2. After this you have the NO but then and already NO_2 is pretty high (Refer Slide Time: 26:08 min); was the NO_2 high when started? It was high in the relative sense. Do not forget that I also have the additional mechanism now in place for converting NO into NO_2. What is this additional mechanism? What I am talking about is converting NO into NO_2 other than ozone. HO_2. Where the HO_2 has come from? It is come because I have put in the system - formaldehyde. I have changed the things here.

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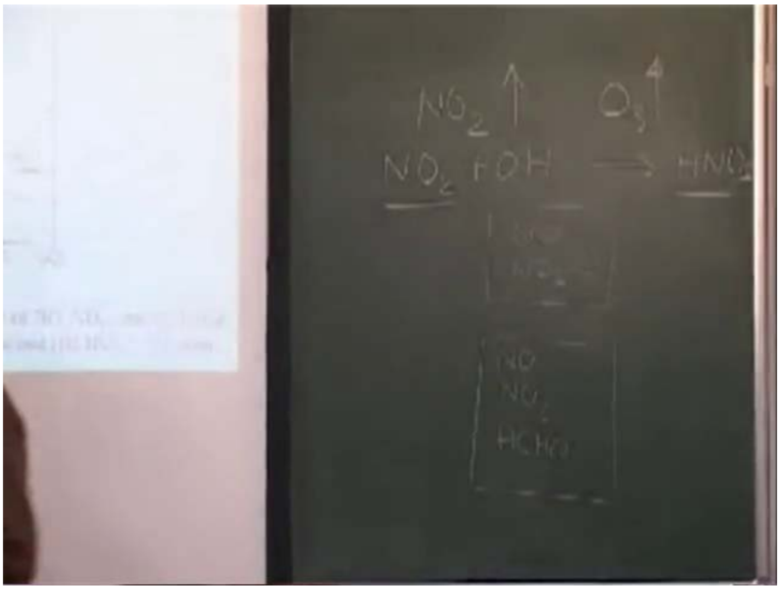

I am not talking about the same box; I am not talking about a different box (Refer Slide Time: 26:48 min). I have more and more conversion of NO_2 and then if I have higher NO_2, conversion is higher. Two things can happen here. If NO_2 is going up it can either increase ozone – certainly possible, but then I should also not forget from my chemistry that if I have the OH and also high amount of NO_2, it can take this NO_2 out of the system and form HNO_3.

As a result NO_2 is also being removed; it means the rate of removal of NO_2 is much faster than the rate of formation of NO_2. If the rate of removal of NO_2 is faster, what will happen to my ozone concentration after sometime? NO_2 is being taken out, my formation of ozone will tend to stabilise; because, every time I want to make more and more NO_2, more and more ozone, I should have more and more NO_2. Unfortunately my NO_2 is decreasing so at some point ozone again started; with time it will tend to stabilise or may even come down or make some kind of steady state or it is reaching at steady state.

Now we use another model and this time at least the model results we are able to explain and how the things are happening. Now, question for you: If suppose I am also measuring here HNO_3 what will happen? It will decrease.

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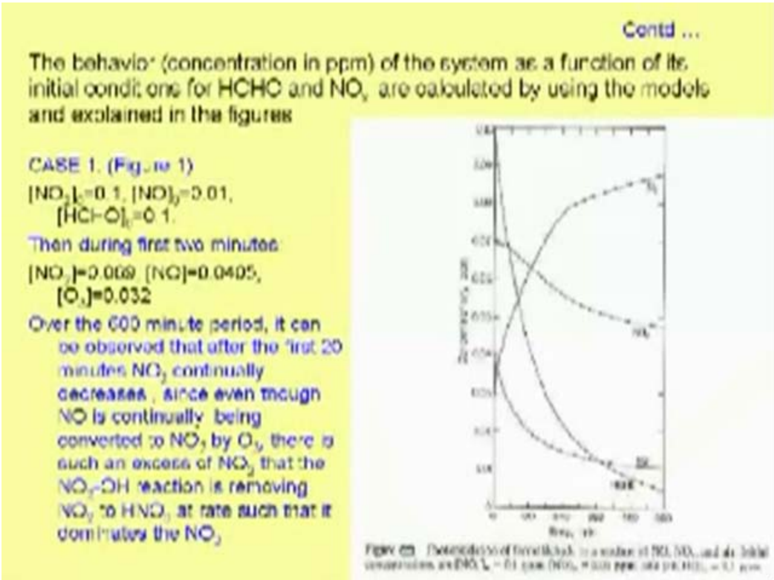

It will start from zero, it may not pick up so much here and then it will pick up something and pick up more; because, of NO_2 is decreasing, NO is decreasing, ozone is stabilising; so it means I am going to where there is more of removal of that. This is how we should use the models because we understand the mathematics, we can solve the equations and we should be able to say as to how and why the behaviour will be the way it is. Whatever science we are learning here, this science is not for learning and passing the exams, but to eventually apply the understanding to solve problems. Let us solve the problems of ozone formation. Someone might be interested in reducing the NO - HNO_3 formation is an issue; because, it is not that we just read it and you know put it because the models are done, the science study, people publish the things, but then somebody should be able to use that one.

What is that you learnt if I want to reduce my ozone formation? What should I do? Control the hydrocarbon HCHO emissions from the car. Sounds very funny! What I can say is that if I could control the hydrocarbon emissions from the car, my ozone levels will come down and that my chemistry says, my science says and my model says; otherwise ozone, I cannot control ozone in the atmosphere. What can I control? Either control NO or NO_2, which again will not be very easy for me to control them, but what I can do is, I can improve my combustion, try hard and then I can improve my combustion, so my HCHO emissions will reduce; hopefully that reduction will result in reduction in ozone concentration. So we all take the decisions based on science to make things better. So do not think we just learn something in class; people indeed use this knowledge.

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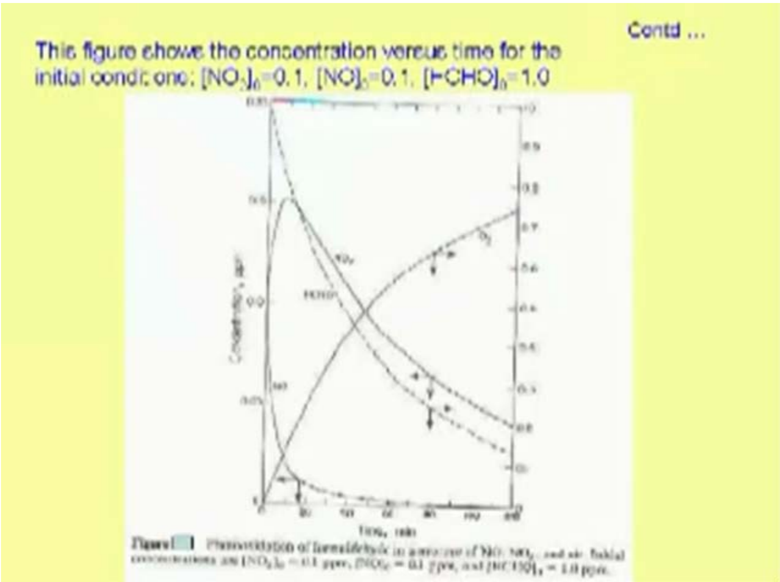

Moving on to case two. What is happening here? Initial NO concentration increased; very high NO concentration. What will you see here? If my NO is high, this of course will break; if my NO is high, then conversion of NO to NO_2 will be very quick the reaction required, slightly the NO_2 will go up.

NO_2 will go up and then it tends to start decreasing and you see here the NO_2 may peak because that time this one overwhelming reaction but this time I have the NO is large (Refer Slide Time: 31:52 min). See the difference? That time I was dealing with small NO quantity that was 0.01. Now I have the high NO quantity; so now, if I have high NO and therefore as you have some oxidizing thing, this NO will be quickly going into NO_2. Once you have the

NO_2, it will decrease by two routes. One is forming HNO_3 and one is breaking down to form ozone. So ozone goes up constantly, NO is constantly coming down, that we can see here. Then, finally, HCHO will constantly go down. HCHO has to go down; there is no other way it can go. Here, because I have the high NO already in place, let us not forget that I have the high NO; then as a result high NO will be converted into NO_2 quickly and then as a result I will have high NO_2 concentration till things become stabilised and the other things start picking up; NO_2 becomes so much as that it is picked by ozone and things like that.

Finally, NO_2 has to reduce, NO has to reduce, ozone has to stabilise as these are reducing. HCHO goes down because that reaction that we have seen, HCHO will continuously decrease. So here the higher concentration of NO that you can see the differences to what will happen. May be your atmosphere is this or may be your atmosphere is something else; still, you can model the things, of course, in the limited contacts of the 4 pollutants that we are talking about.

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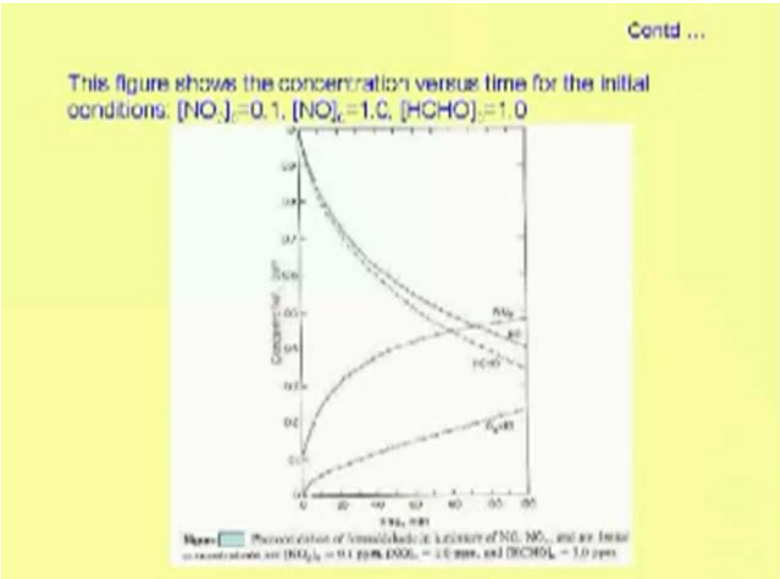

Take another example here. What we have done is increase more NO. What happens then? So we had that peak here, then that peak is still building up. Here NO_2 is going up, I have more NO.

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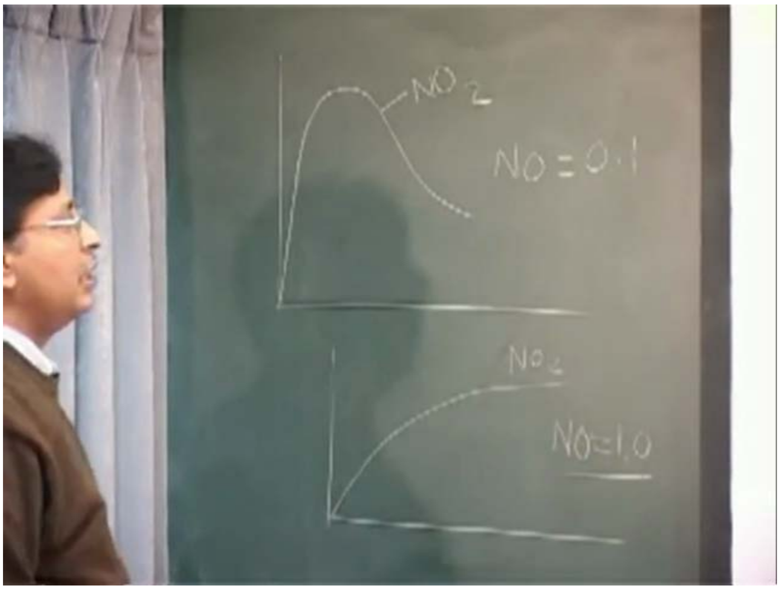

When NO was high, this was the NO_2 and then start decreasing; this is like NO_2. I increase more of NO, and then it is still increasing. This is NO_2; here NO was 0.1, whatever the units mostly in the moles, and here NO was - tell me what was that? 1.0; that is correct. So you see the difference that we are we are making here; ozone will be formed anyway, HCHO will come down. HCHO will always be coming down and will always be oxidised. You see the model (Refer Slide Time: 35:02 min), how the initial concentration can change and the time scale here probably should be the same I guess. The time scale here is a little bit more, but here the time scale is same - 120 minutes; here also time scale is 120 minutes (Refer Slide Time: 35:15 min). You can see here that photo oxidation of formaldehyde is in the mixture of NO, NO_X and initial concentrations were this.

Quickly, the conversion of NO to NO_2 is the formation of ozone is therefore driven by HCHO. That we have seen. Hence product HO_2 thus the theoretical maximum ozone concentration could be produced by this system.

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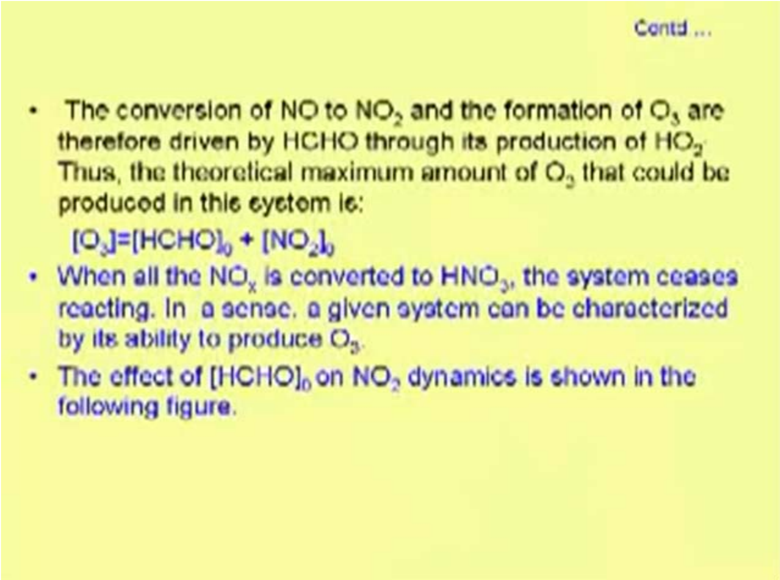

HCHO initial concentration will be determined by this and this. When all the NO_X is converted to HNO_3, the system ceases to react; because, that is a path that we are having, in the sense a given system can be characterised by its ability to produce ozone. The effect of HCHO on NO_2 dynamics is shown in the next figure and that we will show you here.

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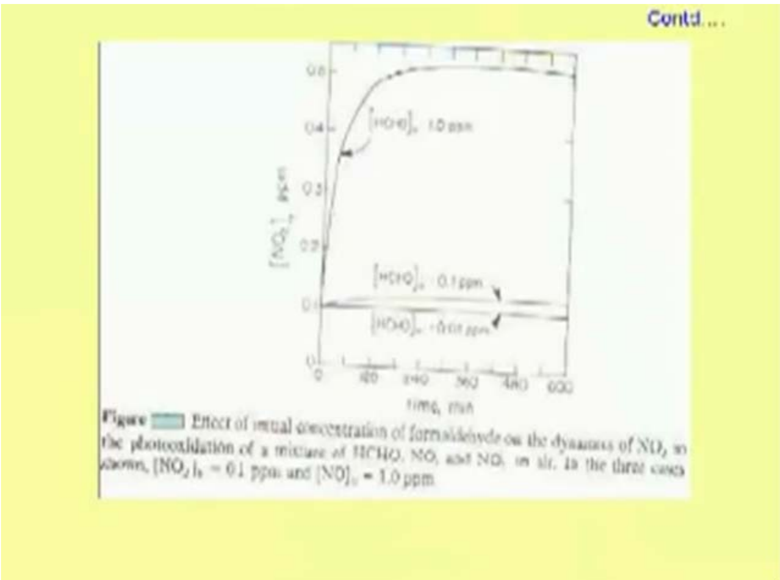

You cannot see it so much. This side is... I do not know if you can see, this is NO_2. This side is your time and this side is the concentration of HCHO. As you increased from 0.01 because earlier we had fixed the HCHO, here we will be increasing; this is 0.01. You see some NO_X, which NO_2 being formed. If you increase much more and you see more NO_x, more NO_2 – let me not call it NO_X; if more NO_2 is formed, then more ozone is likely to be formed.

We cannot undermine the role that hydrocarbons play; the role that HCHO plays and this is how extremely important it is for us for to do some control measures and to understand the complicacy of the system. Let me tell you: things are not so simple. It is just not... I repeat again and again, atmospheric chemistry is a subject in itself, you can be you can be trained on this for the complete semester, but we will do it very briefly here. I am very sure that you are getting a little feel why ozone is high and why things are increasing and why things are decreasing and things like that. If you have to make some kind of impact onto the atmospheric control or control the ozone pollution, ozone is a serious pollutant, let me tell you again and again.

We also need to understand the hydrocarbons; otherwise, hydrocarbons would also be governed by their own impact onto human health. Eventually you will see the control that needs to be done, whether this is to be done, which is the critical: is it the HCHO level which is critical? Or the level of HCHO which is forming the ozone is it critical? And that is how you decide your air quality standards. HCHO, for example, we have talked so much about the standards.

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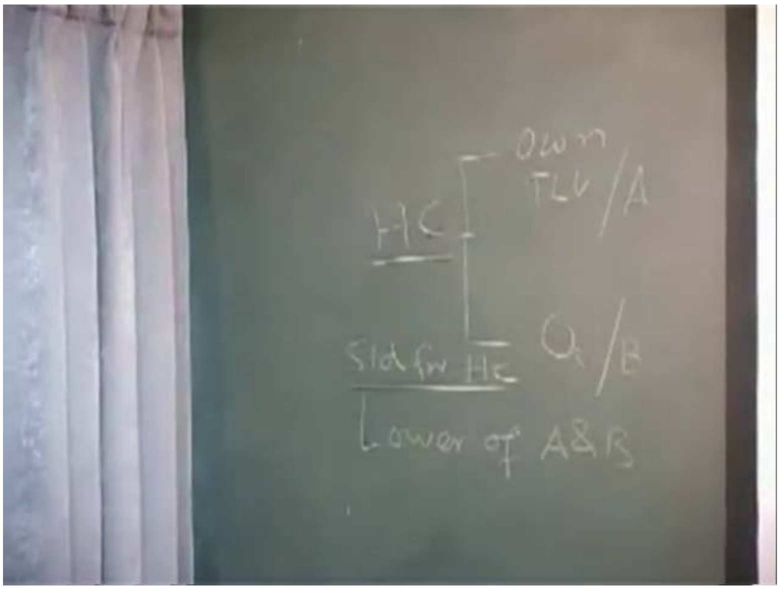

For example: hydrocarbons. One is TLV, if I can use the term - own TLV - or that sort of thing, but this may be a concentration - let us say A. This also has a potential to form the ozone and that ozone concentration is... to maintain this concentration, I need the concentration B. So my standard will be lower of A and B; standard for hydrocarbon will be lower of A and B. Did you understand what I said? So that is what we use all these things to say what should be the standard for hydrocarbon. So it is not just governed by its own harmful effects, but it is also governed because it has the potential to form the ozone. I want to fix the standard for ozone, so for this standard what should be the B? This is for its own value, what should be standard A? Then well choose out of these whichever is lower should become the standard for the hydrocarbons or for any pollutant which has a potential to form something else in the atmosphere. Let us talk about methane. This is something similar but more complications come as you have the higher compounds.

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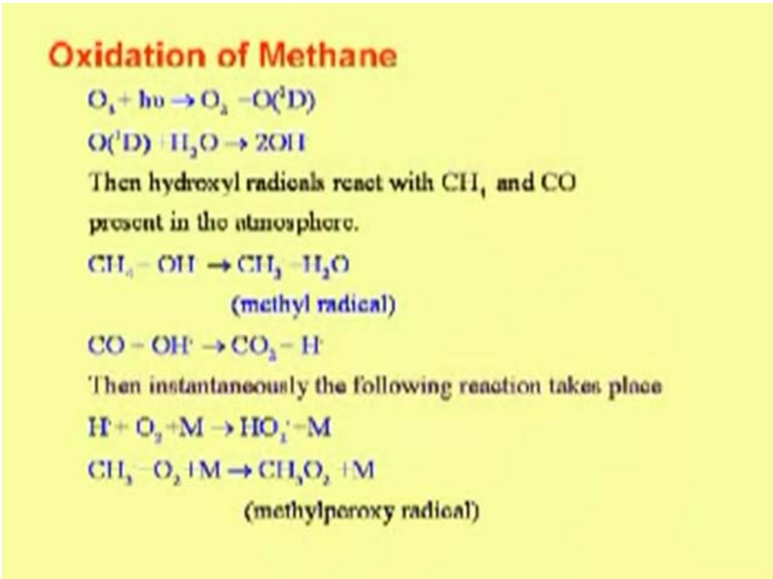

We all are aware of that. You know the sources of methane and generally methane does not come out from the cars and scooters. We have enough sources of methane and methane concentration is always significant. Methane is not so harmful in the atmosphere but and it is a very stimulus compound methane like is carbon monoxide. It reacts with OH. OH can make everything react. So all the time we say it is OH radical and so is again referring to the presentation given by the Ravi Kant Pathak, see that he was talking about OH radical. OH can make methane methyl radical. This is again from the past as we have done here.

Let us see what the methyl radical can do. It can react with oxygen and makes CH_3 O_2 radical which is methylperoxy radical. Now we have to see what this methylperoxy radical can do? Because the reason is methane is in plenty and this can also produce CH_3 O_2 radical. There is a little dot that you see here and then the chemistry of the methylperoxy radical is... So, it is not only HO_2 that we are referring again and again the many ways the NO could be oxidised.

The moment NO is oxidized to NO_2 we have the two ways. Two things that might go on, two things will go competitively is a formation of ozone and formation of HNO_3. The major routes for NO_2 is either form the ozone and to exit. In a way we are answering the question that we raised - that why the model failed? The model failed because we had not considered methane, formaldehyde, carbon monoxide and then in a larger model we should consider all these things. You have already seen the complexities that will come in the model, all the Ks and things like that; solving those equations with respective time variability.

How many of you understand the numerical modelling? Numerical modelling is one of the ways, sometimes it is the only way of solving. All of you know how to solve ordinary equations and algebraic equation in terms of x, y, z and p, q, r, s. I have that many variables and then I can write then as many equations and I can do this one, but what you can see from here, all these equations that you will see and that you will write there it will be in the differential form. Then they will be like the way in which we solve simultaneous equations and algebraic equations. In this process of the modelling, I do not know how far we will go in that, we will write many differential equations and to solve these differential equations, we do not have the ways and means to solve them completely. So we resolve to something called numerical methods. I am not sure how far that we will go into the numerical method in this course. Probably not but you should know that these equations are solved numerically.

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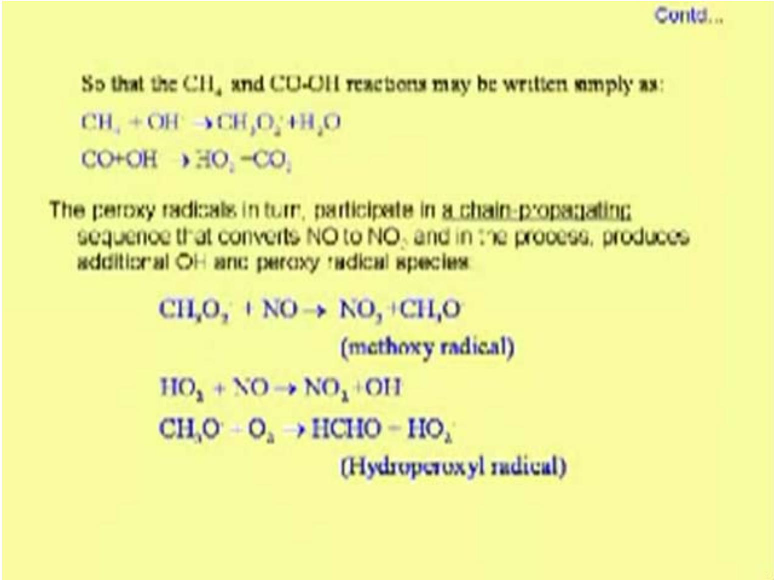

I might do some example for the numerical methods, but that is how you solve these equations. Then you can really show the time functions and all the equations, how the reactions are changing up and down. Let me tell you, people have done numerical modelling with hundreds of equations going into the modelling process. I have the metrics of the 50 by 50 algebraic equation - what is the method that you follow? Cross elimination. It is a very powerful method.

You are using the cross elimination method, you can also write these equations and you can you can numerically solve the equations for various small delta c and delta t. You can write delta c and delta t for every step or the time scale and then you can put these numbers in cross elimination and solve it iteratively every time. This is how the numerical methods work. So these all equations are solved numerically generally and that takes a lot of computer time. The same thing we will repeat here in a competitive reaction and now we are coming to something else. See the process that is also a possibility.

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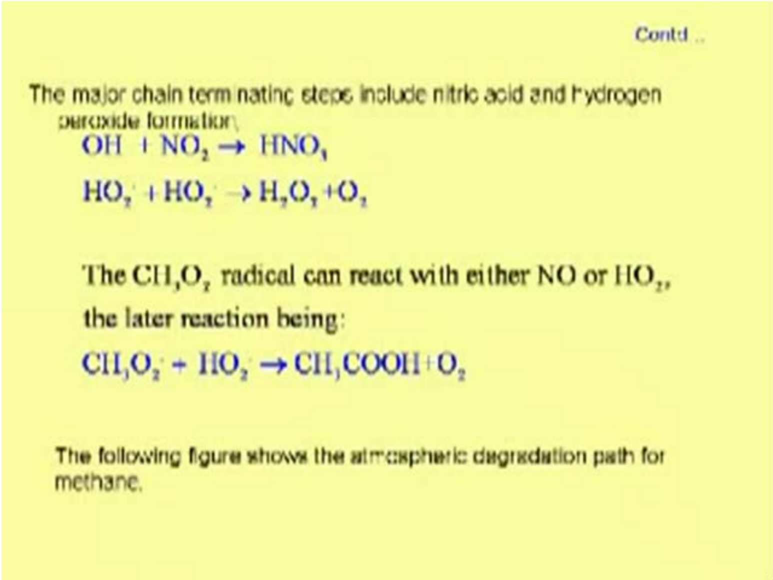

We are finding lots and lots of HO_2 but these HO_2 can also combine to give me hydrogen peroxide. We do get a reasonably good amount of hydrogen peroxide and what type of special combined H_2O_2 is? Combined H_2O_2 is highly oxidizing. You have got something more which can oxidize something else and in fact the oxidation of SO_2 by not only the vanadium pentoxide but also H_2O_2 is very significant. I do not know how much you know....

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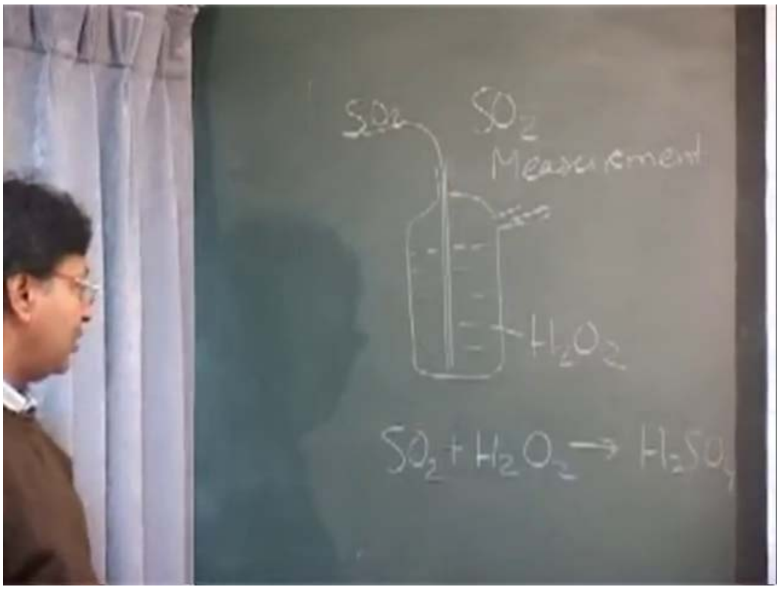

When you want to measure SO_2 from the stack or in the atmosphere, you take H_2O_2, this may be outlet. Put SO_2 in there; this SO_2 will quickly make H_2SO_4. Is it balanced? It should be balanced. H_2SO_4 you can do its iteration in the standard alkali and can find what the amount of sulphate is? Once you know the amount of sulphate you, can find out what was the SO_2 concentration. In fact, this is the way. So you see how H_2O_2 is formed in the atmosphere. Who can think of this and this H_2O_2 that is found in the atmosphere and this H_2O_2 found? As such life is not simple.

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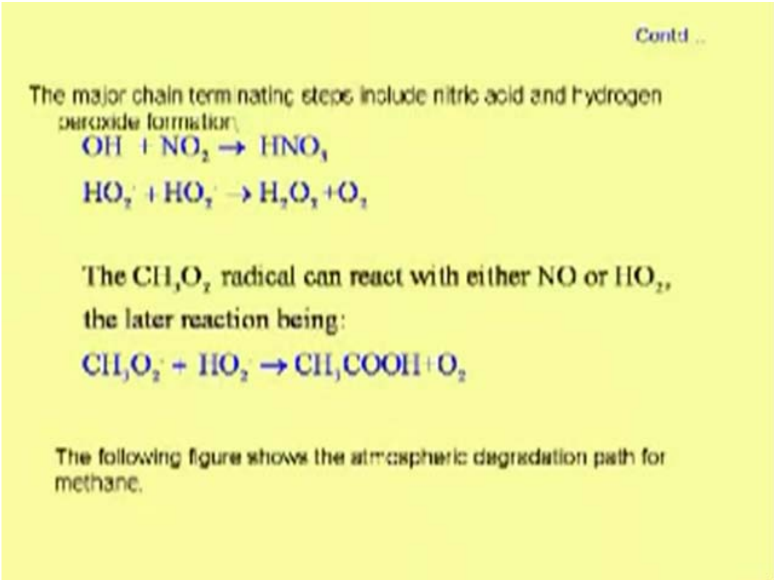

HO_2 is hydroperoxy radical, which is very important for the formation of your NO_X. It can also react with this CH_3O_2 radical either with NO or with HO_2. Then if it reacts with HO_2 it produces acidic acid in the atmosphere. These reactions are physical reactions; we are not talking somthing, let us try out something and something will be found; now they are found. People can measure this and you see which we have not thought that it can even produce the acidic acid concentration.

So do not forget that HO_2 is just not oxidising to NO_2, oxidising NO but it can also react with the CH_3O_2 radical to form this, to form the acidic acid. We are also producing H_2O_2 in between which can take up some other reactions in the atmosphere. It can oxidise many more things but H_2O_2 is one thing, but of course we are not talking about the phase this can happen, this can happen in the vapour phase. SO_2 may be in the vapour phase but this H_2O_2 has to be in the liquid phase. It may be liquid phase or this may be observed onto the particles and the reaction can occur onto the particle surface (Refer Slide Time: 49:02 min). We will not get into those details but of course certainly these are the topics for research. We will stop here.