Environmental Air Pollution

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Lecture No. # 9

Atmospheric Formation of Air Pollutants - 3

It is time to summarize a few things and then give some kind of meaning to chemistry that we have been studying; also, to answer as to why and what will be the ozone levels really be having seen so much of complicacy in the things. It is a very much generalized of the version that we have done so far. Let us have a quick look at that.

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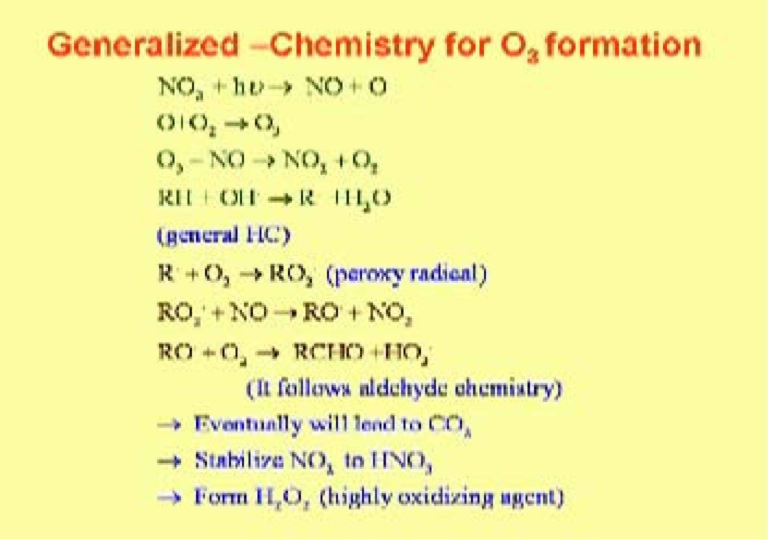

Generalized –Chemistry for O_3 formation

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 \rightarrow O_3$

$O_3 + NO \rightarrow NO_2 + O_2$

$RH + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$

(general HC)

$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (peroxy radical)

$RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2$

$RO^{\cdot} + O_2 \rightarrow RCHO + HO_2^{\cdot}$

(It follows aldehyde chemistry)

→ Eventually will lead to CO_2

→ Stabilize NO_x to HNO_3

→ Form H_2O_2 (highly oxidizing agent)

Nothing new about this; nothing new about this; this we all know, but what new thing that we have learnt in few lectures is this reaction: that hydrocarbons do react with OH radicals. There H_2S is formed and the radical - generally the alkyl radical - is formed; that can react with the oxygen to make the peroxy radicals – that we have seen; these peroxy radicals can either produce HO_2 or they themselves can oxidize the NO.

If you recall, what was the chemistry of methane? What happened in the case of methane? What peroxy radical did we make last time? CH_3O_2 - methyl peroxyl radicals. What did that radical do to NO? It reacted with NO to form the NO_2. In turn when we are reading about the NO, reading about the CO and other hydrocarbons, it was forming the HO_2; hydro peroxyl radical - HO_2 -can quickly react with the NO to produce NO_2 and [ ]. So we have two mechanisms. Bottom line is that it is that the hydrocarbons that we have so many in the atmosphere, it can make the peroxy radicals, it can make the peroxy radical in terms of the basic compound; that example was a methyl peroxy radical, that is CH_3O_2 or it can make HO_2 that is the hydro peroxyl radical. Though, eventually, what they will do? peroxy radicals will oxidize NO into NO_2 and we get lots of NO_2; once we have lots of NO_2, we get lots of ozone.

Therefore, ozone is not only just produced by these reactions, they are produced by this reaction, but the source of NO_2 is simply not this reaction. This is what I wanted to say – that the source of NO_2 is just not this reaction; the source of NO_2 is this reaction triggered by the photochemistry and triggered by the hydrocarbons that we have.

There are many more things in this, but you see the basic thing that we want to answer is the question of ozone, because, ozone was one of our criteria pollutants; it caused lots of problem; gives lots of difficulty and then it caused lots of problem in the lungs. So ozone measurement becomes important. And why we had to study so much? Because the ozone is a secondary pollutant; had it been primary pollutant - go to the factory, go to the car, fix it there. We cannot fix it in the car, we cannot fix it in the ozone in the power plant, because, they are not generated from the power plant.

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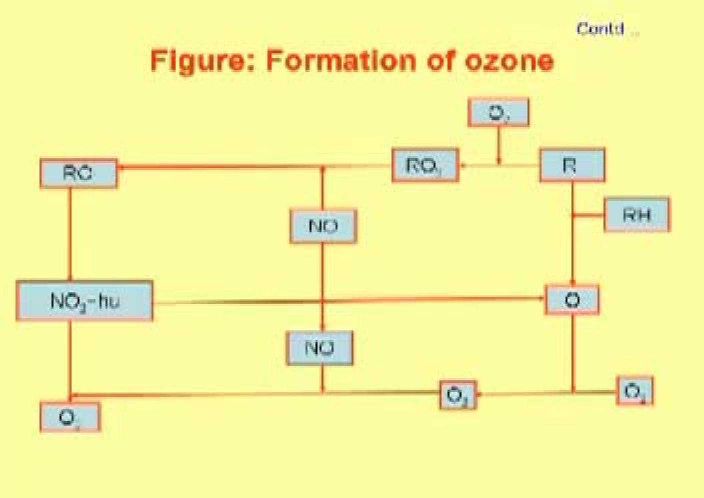

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Figure: Formation of ozone

This slide is again in the form of summary, to give you more feel of the overall system. This will be much easier for you to remember; of course, some basic chemistry you have to remember. It does not matter where you start from. You have some NO_2 that can break down into this radical H_{mu}. This can be broken to NO and NO can go two parts, but this NO can be come from breaking of this one or the NO here can be very much the primary source that has been generated.

If we start from NO, we can follow two routes this way or that way. A part of NO comes from here, but this part definitely will give you some NO and some oxygen here - atomic oxygen. This atomic oxygen what state is it in? Nascent oxygen, but in the ground state or excited state? Ground state, because, the ground state, O will react with oxygen; if it was in excited state it cannot react with oxygen. Since it is not in excited state, therefore, we will not form ozone, we will form rather OH radicals. And if we are not forming the OH radical, nothing will happen in the atmosphere. This will form this one and the part of this will be in the excited state. Therefore, we go the other way; that cannot combine with oxygen. This is the summary of what we did.

We have the hydrocarbon that is coming up here reacts with this O or OH radicals and it forms…. It breaks down to alkyl radical; that reacts with oxygen to form the hydro peroxy radical. Hydro peroxy radical either as a hydro peroxy radical or the peroxy radical - it can be RO_2 or it can be even HO_2; that can react with excess of NO which you have, lots of NO in the atmosphere, react with this thing and eventually this will become RO, but what you will get is the NO_2. You will have lots of NO_2. If you recall, in the first the first lecture, when we were talking about the atmospheric chemistry, we were simply talking about this route (Refer Slide Time: 06:41 min); you had modeled this route; we had not considered that route (Refer Slide Time: 06:51 min). If you consider this route as well, then, of course, you are producing more NO_2 and more NO_2 means more ozone. Most people started considering these things – the model started fitting the observed concentration.

Always remember that what you do in theory should be checked with the practical thing. Now the people who do most of the experiments are talking the other way. They are saying: what ever you do in the practical, or whatever the observations you get in the experiment, we must look for the theory to explain that. Obviously, we do not want to deal with the things in a black box mode. When you have got the experimental results, they you can say: if this is high, that is high. The question is – why? Science is all about asking - why? Of course, the experimenters used to say: Oh! Well in theory, you can do anything, but see what happens practically. Now, the people in practical say, we are observing it practically, we are finding it through experiments, what is the theory behind it? And the theory or the science what you do in your M.Tech thesis is the theory or sometimes we use - what is the mechanism? All research is about mechanism, to understand the mechanism. This is the mechanism (Refer Slide Time: 08:11 min).

Having said this picture in a very, you know, in a very simplistic way, the reactions that we are talking about, the R(s) here (Refer Slide Time: 08:18 min) hundreds and thousands of R are there in the atmosphere. It is almost impossible for us to sit down in this room and just simply do something. People will, with all the computers that they have, run very huge models, where they can consider all these species, their rate constant and their chemistry behind it and then with the time variability in the mind, they can model the full thing. Those models people have done and then they had tried to explain what the variability is, what is the scenario of the ozone that you get. We will come to that, but there is something more that happens, other than the ozone. That also is a very serious or a very important part of chemistry and also very important pollutants.

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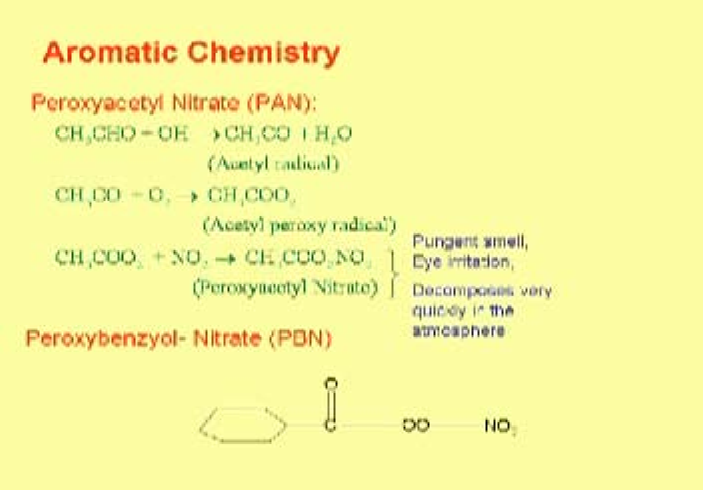

Aromatic Chemistry

Peroxyacetyl Nitrate (PAN):

$CH_3CHO + OH \rightarrow CH_3CO + H_2O$

(Acetyl radical)

$CH_3CO + O_2 \rightarrow CH_3COO_2$

(Acetyl peroxy radical)

$CH_3COO_2 + NO_2 \rightarrow CH_3COO_2NO_2$

(Peroxyacetyl Nitrate)

Pungent smell,
Eye irritation,
Decomposes very quickly in the atmosphere

Peroxybenzyol- Nitrate (PBN)

I am sure that sometimes you go in the area, there are emissions and you know like your eyes burn, because, many of the species, which are found in the atmosphere is that simply not ozone. See here, peroxyacetyl nitrate - in short form it is called PAN; PAN is a serious pollutant; short life of the PAN is very small; it can [decompose] quickly. So this what we are forming - from what ever aldehydes you can think of, reacts with OH radical and it forms the acetyl radical. This acetyl radical can react with the oxygen and form acetyl peroxy radical. This acetyl peroxy radical, O_2 as you see, acetyl peroxy radical, that can react with NO_2 and this particular thing (Refer Slide Time: 10:01 min) can combine NO_2 along with this one. This is a very special reaction you know; so it can react to form what as we call it as PAN.

People have measured PAN in the atmosphere, pungent smell, eye irritant, makes you very uncomfortable, although decomposes very quickly. We will not go into the details, but you see, if you go somewhere, they ask you: have you done the course in air pollution; they say do you know what PANs and PBNs? He himself probably would know to this extent only. You are sure: yes, PAN and PBN are the photochemical compounds from the atmosphere which is part of the smog that we see sometimes because of photochemistry; PAN and PBN are very serious pollutants. PBN, as said, well you have the more aromatic than benzene and then the NO_2 combines with that one. So what you are doing here is basically this thing (Refer Slide Time: 11:03 min) is replaced by the benzene and one hydrogen atom; that is where the CO is coming. So this is called peroxybenzoyl nitrate. That is the name given to this.

This is in the PBN is also serious and PN formed is more than compared to this one (Refer Slide Time: 11:20 min), because aldehydes are there and this is also found in the atmosphere. Just for your knowledge, you should know: What is PAN? and What is PBN? These are the problems, but the control of them, these compounds are only control of the hydrocarbon species, which people do attempt for the hydrocarbon species.

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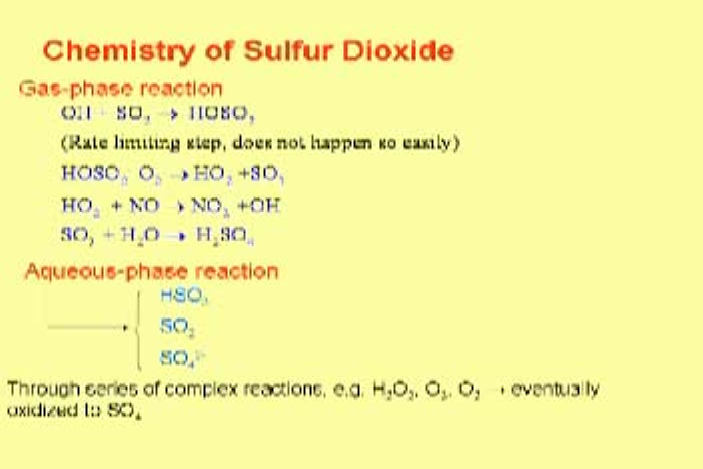

Chemistry of Sulfur Dioxide

Gas-phase reaction

$OH + SO_2 \rightarrow HOSO_2$

(Rate limiting step, does not happen so easily)

$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$HO_2 + NO \rightarrow NO_2 + OH$

$SO_3 + H_2O \rightarrow H_2SO_4$

Aqueous-phase reaction

$\longrightarrow \begin{cases} HSO_3 \\ SO_3 \\ SO_4^{2-} \end{cases}$

Through series of complex reactions, e.g. H_2O_2, O_3, O_2 → eventually oxidized to SO_4

Let us quickly talk about SO_2 very briefly, because, we have to cover many things. OH Radicals – reactions happen in both in the gas phase as well as in the aqueous phase and also on to the surface of the particles for SO_2. So, OH radicals, you can form the… it can oxidize sulfur dioxide to HSO_2. This thing is the main reaction (Refer Slide Time: 12:10 min); rest depends on to this one, while we are talking about the gas phase reaction (Refer Slide Time: 12:18 min). This can combine with oxygen again and give HO_2 plus SO_3; HO_2 is again hydroperoxyl radical - important for us. It just appears again and again, but SO_3 what you are seeing… SO_3 is always remember, SO_3 is highly reactive; it can instantly combine with water. In fact, it will be very difficult, not so easy at least you know like to measure SO_3, because, if the moment it is in the moisture it must produce sulfuric acid; that is what you are seeing here (Refer Slide Time: 12:51 min).

If you recall we also had given the aqueous phase reactions of sulfur dioxide. I also recall we were also making hydrogen peroxide in the atmosphere; how did that happen? How did we make

H_2O_2? How was the H_2O_2 formed? Lots of HO_2 that we are getting. HO_2 and HO_2 can combine to produce H_2O_2.

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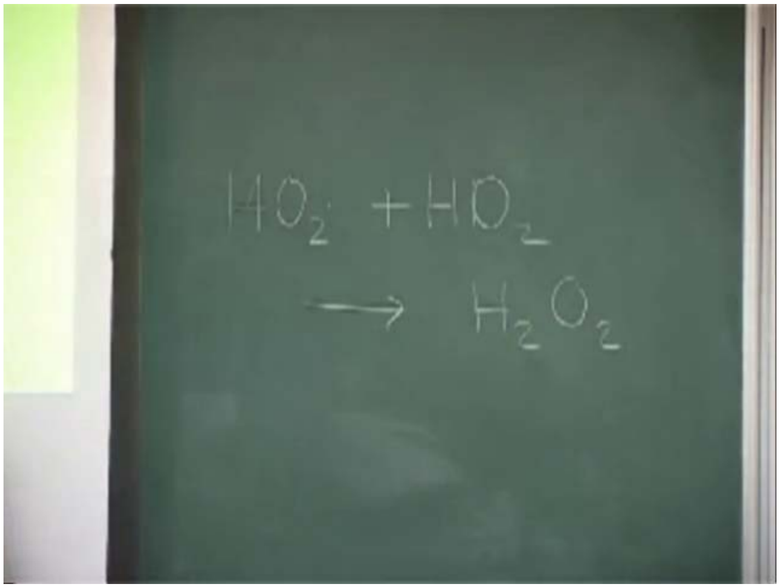

This H_2O_2 is particularly important for oxidation of sulphur dioxide, but in the aqueous phase, because, the water vapor is always there, some condensation takes place on the surface of the particle and this H_2O_2 is very good in oxidizing SO_2.

Once it oxidizes, you know, it forms sulfuric acid. I gave you the example; I even showed you that one of the techniques for the measurement of sulfur dioxide is absorbing the SO_2 into H_2O_2 and that will produce sulfuric acid almost instantly. You can convert this first into SO_3 by the oxidation and then eventually you will produce this acid sulfuric acid. You can see the aqueous phase is sometimes much more important than this one. Apart from the aqueous phase, there is also the reactions that can occur on to the solid phase.

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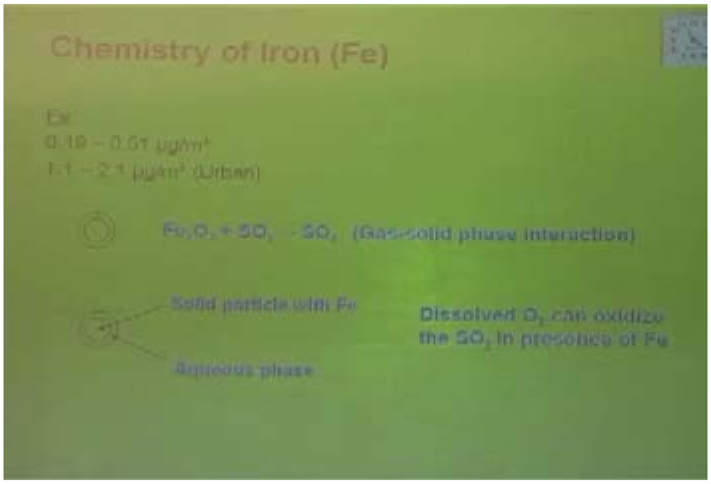

Chemistry of Iron (Fe)

Fe

0.19 – 0.51 μg/m³

1.1 – 2.1 μg/m³ (Urban)

$Fe_2O_3 + SO_2 \rightarrow SO_4$ (Gas-solid phase interaction)

Solid particle with Fe

Aqueous phase

Dissolved O_2 can oxidize the SO_2 in presence of Fe

Iron acts as a as a catalyst and also as a quick it fastens the oxidation of SO_2 into sulphates. This is the level which you might get in the rural areas, but in urban areas, the levels are very high, almost 2.1 microns; it is not a small number. Source of iron can be largely be what? The factory dealing with the iron smelters, iron processing, [ ] and if you recall the [ ] furnaces and things like that and what else? What are the major components of the soil? Silica is there, aluminum is huge and iron you know is small. This iron also you will find very easily even in the rural areas. So, this SO_2 can also, you know, there can be little moisture as well as here and then the SO_2 can envelop the whole thing and the reaction can occur; as a result you can form the sulphates.

You can almost have all kinds of reaction: gas-to-gas, gas-to-liquid and gas-to-solid phase reactions also. Dissolved oxygen can be oxidized once you are in the aqueous phase because you also can have the aqueous phase right over here (Refer Slide Time: 15:59 min). Then you can make the SO_2; the presence of iron can go into the sulphates and you can form the sulphates. Obviously, if your atmosphere is rich in this one, your atmosphere is rich in (Refer Slide Time: 16:14 min) photochemistry as you see we can form a lot of H_2O_2. So many times people will say: Oh! Sulphur dioxide levels are low; there is no pollution from sulphur dioxide, but they do not know, then they try to do mass valence of sulphur dioxide; it does not fit; we are emitting so much of SO_2, but when we compare with SO_2 levels, what we get in embedded air are very low. Where is SO_2 going? SO_2 going to sulphates.

So, when you want to look at the mass balance of sulfur dioxide and then you want to answer the question - why are SO_2 levels so low? In India, SO_2 levels are really low. One really needs to examine and then say - SO_2 is going into the sulphates and sulphate particles are formed. Then problems associated with sulphur dioxide is translated or transformed into problems with sulphate particles. Thus, we can get the secondary particles also. We will not talk about SO_2 any further because that is enough.

We may talk about the formation of secondary particles; that is what some [student] is trying to look into his study for his PG research: how fast the particles are formed because of the gases as being the precursor gases. There is another M.Tech student who also worked on this. He found out that: the SO_2 levels were low, at the same time sulphate levels were high in India. Then he could explain why SO_2 levels are low and sulphate levels were high. The sulphate levels were many times higher than the SO_2 levels itself. Science is same, but the extent of chemistry in our area, in India, will be very different as compared to the countries that are colder.

Question (by student): How would you explain spatial variability?

The reaction quickly occurs and once you have so much of SO_2, in just a matter of 2 or 3 hours, that most of the things will be converted into sulphates. So, if you are looking at the wind speed, you will find that once the wind has travelled a distance of 2 or 3 kilometers, most of the SO_2, depending on all equilibrium constants, at least 50 percent of SO_2 will be converted into sulphates.

If you are close to source, you will find SO_2, but you are little away from the source you will find lots of sulphates rather than SO_2. That is how you say well the problem may be that of the sulphates, may be not that much of SO_2. Maybe, in the Indian context, we want to measure the particles, we want to measure the sulphate content of the particles rather than doing a great deal on SO_2; because, SO_2, may not be on the […]. The other thing in India is that it is all happening on the surface of the particles. Our conditions are very dusty; we all know that. If you go to North America, particle concentration will be around 30 micron; we may have 300 to 600 micron. So we have lot of particles. Then as a result, the chemistry on the particles can become important for us. So we will get probably more sulphates than what they get. On the contrary, they will also get the sulphate, but in what form? In the form of H_2SO_4, because, they do not have the particles and neutralization; whereas, we will get most of the sulphates on the particles. They may have a large problem of acid rain; we do not have the problem of the acid rain – not so much, because we have a lot of dust. Suppose the particles are alkaline, which is the case in many of our normal areas, if the particles are alkaline, even if some sulphuric acid forms, it will be neutralized by them.

In fact, you will be surprised - a question has come up: what is the ph of the rainwater?

[Conversation between student and professor – Not Audible (20:23 min)] Point something.

Why? Because of carbon dioxide in saturation with water drops and as a result the ph is something like on the saturation level of CO_2, the ph is around 5.6. That is low ph. It does not last very long. It quickly gets backs to the normal ph 7, but the kind of rain that we get in India the ph is like 8.7, 8.8; people have reported ph up to 9 or 9.5. We have the problem of alkaline rain, if there is a problem, rather than the problem of the acid rain; we have alkaline rain, but what is happening with time? Because we are increasing the SO_2 emissions, the particulate levels are either the same or they are reducing; as a result, the ph is coming down. We get the ph of the rainwater anything in between 6.5 to something like 8 or something, depending on the locations you are, but in the country where the soil is not alkaline you may face a problem of acid rain. So that is how these issues are, but let us quickly go to something else. So SO_2 is very interesting.

We have a fairly good idea as to what is happening in the atmosphere and now we want to see as how with time, as our daily routine starts, how will the pollutants look in the atmosphere? Wake up early in the morning and then you are following your daily routine, you go and then around 9:30 AM or 10:00 AM, you see the CO level; lots of traffic and things like that.

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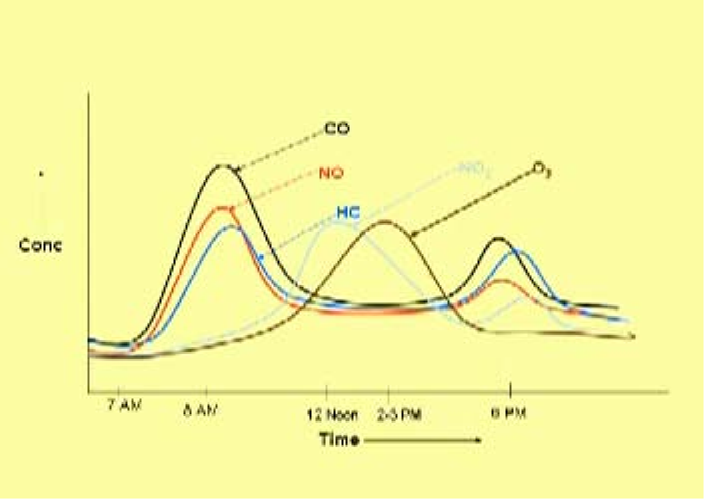

Although we have talked about the CO chemistry, it is still – CO, I would not call it inert – but it does not react so easily. It is so difficult to convert CO into CO_2. The life or half-life or the residence time for CO is high. As you can see, people go for their work, activities start, it goes up; afternoon it reduces, because many of the activities cease and then again in the evening it increases. Always remember the peak in the evening is not as prominent as in the morning; because, you all can understand if people go to their work at the same time, but in the evening people are out in a defused way. It is not the peaks will not be the same.

Let us see what happens to the other species. NO - you will be closely following the source. The question for you is now – How will NO_2 look like? Will it be like same as NO_2 or something else? It will be different. There will be a lag, because, most of the time we are emitting NO and that NO converts into NO_2. Let us see what kind of things we get. These hydrocarbons will be the same as this thing, but let us quickly look at this NO_2. If we are measuring it, we will say – let us capture the maximum concentration. We will measure the sample only for this period, because that is where we have the maximum pollution. Then we will always report that NO_2 is not a problem. We do the science not just for getting a job; we do the science to solve the problems. So knowledge of the science is so important to find the solution.

Of course, NO_2 will peak little bit around 12 Noon or something and then you will see then again may be in the night not so much, but it will little peak a little bit and then again it goes to the normal or low values.

Suppose I am staying in Kanpur on the GT road. People say the no entry opened after 8 'o' clock. [Audio not clear (25:02 min)] What will happen if I am looking at, for example, NO? Let us have a look at this. This little reddish line. So after 8 'o' clock I may get little peak here, because, trucks cause lots of NO and what will happen to the NO_2? NO_2 will not peak so much as the NO will do, because in the nighttime, all the reactions that we have talked about are not likely to occur. Something else happens; that probably we will talk about or may not talk about. But what do you see, is this is the truck, you see the NO levels going up a little bit, especially on GT road. NO_2 picks up but not so much; NO2 will not go so much, because there is no one to convert the NO into NO_2; largely reaction in the ozone. Ozone also will disappear we will see the how the ozone will disappear and now I want to plot for ozone now. How will the ozone look like? Just tell me at what time ozone is likely to peak? Afternoon, after NO_2. So if you want to measure the ozone it will be around maximum around from 2:30 p.m. to 4:30 p.m. In fact, this should be a little bit on this side. [Audio not clear (26:45 min)]

Again, you have to be measuring ozone more if you want to capture the maximum. You also see the variability given in this one (Refer Slide Time: 26:54 min). It again reminds us for the point, if you recall, we have said - the standards should have the averaging time. If the ozone has caused problem at this level and I am looking at the average ozone level, I say – the average level is above this 10 ppb; where as, the damage is already done. So, for ozone, you should have the short-term standards. I do not know if you recall we gave the ozone standard should be 1 hour standard.

For example, things which are not showing know so much of variability or which should not have the immediate impact in terms of the health, then you can go for the longer average time, but ozone will always have the shorter average time. So this should have a shorter average time. So the little thing that we should know and understand should help us in not only putting the measurement device, but also making the standards. We should know when to measure, what problem will occur and so on.

This knowledge also helps you, for example, some somebody is working under you; they come from the data; you should always have the habit of looking at the data. You should ensure the data makes sense. For example, you can say how can UDV be less than VUD? You quickly find out. So it was all right you have done the measurement of ozone. Ozone peaks at 2 'o' clock. It tells you two things, if suppose ozone peaks at 2 'o' clock - either the measurements are wrong or you have something to discover. Something more which you do not know is probably happening. It is always important to look at the outlaying data. The data within certain range which you know, sometimes do not tell much. Something we look outside the normal range; that should open your eyes or excite you. You should say either something wrong – you are doing a terrible thing in your analysis part or there is something more of science that you have to learn. Maybe there is a local source or something.

We will tell stories and this is a nice story. We were looking at the data for carbon monoxide and we were finding the same pattern as you see here. This is a traffic intersection in Delhi.

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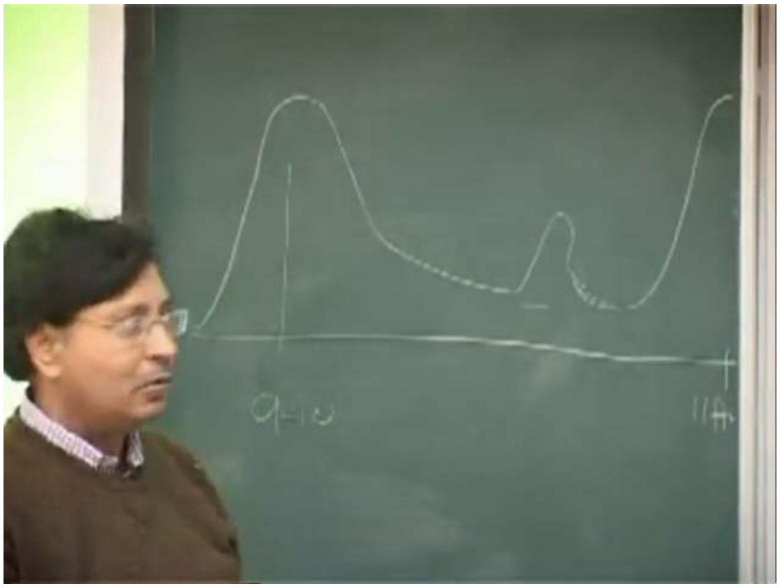

This is at morning 9 'o' clock or 9 a.m to 10 a.m. Then it peaked, then small peak and almost peaked; then it disappeared; then at night 11 p.m. again peaked. In the heart of Delhi, you can image that all the sources were probably disappearing; then traffic comes to a cease at night. This was an automatic instrument. We could not find any manual errors that can happen. We could see the peaks clearly. We did not know what was happening. We thought of all the science and science did not help us. Sometimes it might be a good idea to go to the site and see what is happening at 11 ‘o’ clock; we are going to the site to measure it. In fact, we did go there. Especially this was wintertime; so season becomes important. The wintertime, any traffic intersection, there are lots of offices and commercial areas, and things like that. We were there at night 11 ‘o’ clock and were trying to observe what was happening there and why the instrument should suddenly show the high level. It was wintertime, there were lot of commercial buildings and all the chowkidars who were there, they come out to a central place, it was so cold, they will fire anything and everything that they have; the buildings are left to God to take care of; they will coolly sit down, they will be talking nice heat and they will be cozy and comfortable. The sampler, the cup which was sampling the air, was right above the spot where they were doing all this. So the level will always go up. It was so small - the fire. That was reason, we found out; that satisfied us. It was not the real thing; it was more because of the local effect. You also have to be very sure that you are not capturing the local effect. The local effect can be anything. You want to measure more in the regional level as to what the larger population is exposed to. We just did tell them - well you can continue to do what you are doing, but move a little bit away like 100 meters from this place and which they did; the levels you know like dropped and became normal. Anyway, that was a little bit of story, but sometimes I remember; sometimes, I do not remember.

The good thing is that you have the watch coming up there. Sometimes the problem with this watch is the clock which you see there. One time there was a clock and then this thing is high. The board was here and the clock was up there. I see the students you know like in the beginning everyone was at this level and after sometime, the level was that sort of thing. [Audio in Hindi 32:34 min] That can also happen you know with the clock there and you see and I say what is happening. Initially the level was high like this and then it is like this; something that you watch on television, you know, the newsreader reading like this. Then I figured it out, they are looking at the clock and nothing else. Now I think they have done a very good thing. In all complexes, the clock is at the back. Now the students turn back and things like that. I could feel it you know; like in the beginning, everything was fine and later on like this.

Let us go to the next slide. Let us see what is coming up. This is the final answer to our ozone issue.

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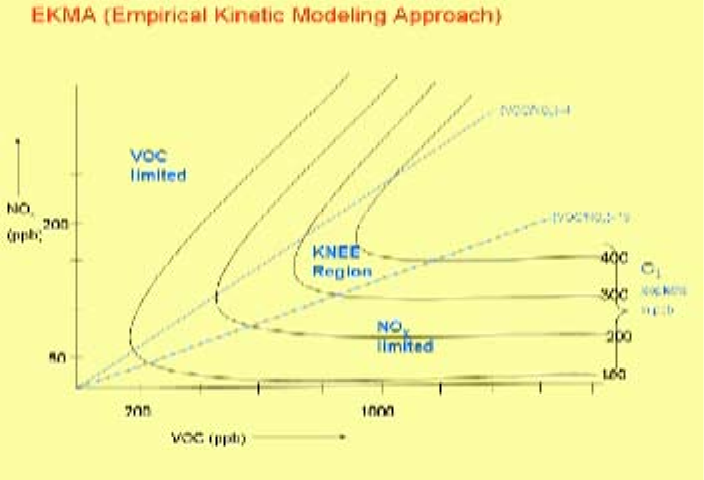

EKMA (Empirical Kinetic Modeling Approach)

These people put into all the science together and into the mathematics and to all the modeling - little modeling that we have done for 4, 5 or 6 equations - the people did the same modeling with hundreds of equations and with their rate constants and things like that. Then they plotted for a particular region as to how the variability in the ozone - these are the ozone isopleths - and this model is called EKMA model. That is empirical kinetic modeling approach. There was science also; lot of empiricism was also there. So one side we plotted volatile organic carbon, let us say in terms of pvb and this was done both experimentally as well as with all the mathematics that they had.

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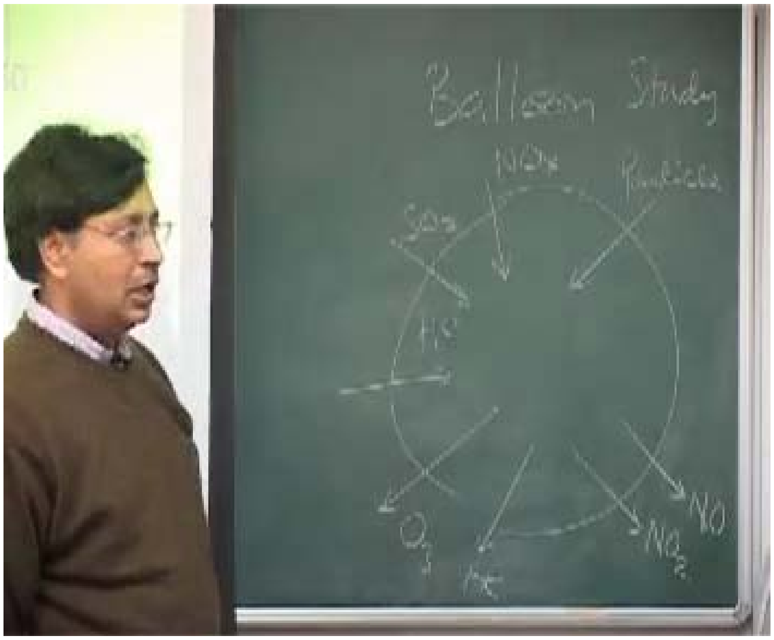

What they did was you cannot vary the things; we call it balloon study. Before the whole thing in UV radiation put everything what is there in the atmosphere: hydrocarbons, SO_2, NO_x and whatever you know the particles, and then you have the sensors coming out for ozone for hydrocarbons; you can [ ] these hydrocarbons; all these things can be done. You can have the other things and you also are measuring the no two $NO_{2,}$ also you are measuring, NO and that sort of thing. Then apart from this experimental data, they also had the mathematics to this one and then they come up with this kind of thing. Obviously, you all can understand things have to be little non-linear and complicated; to model atmosphere is very difficult. They found that the levels are something like this. These are the isopleths. You can see that the levels are going higher and higher. This region, when the ration VOC to NO_x is around 4 – this is called the knee region. The reason why it is called the knee region? It is like your knee; this is called the knee region. If you look at this area, this is called NO_x limited region, because you see here the NO_x levels are low.

Here the VOC levels are low. So VOC levels are low, it means this is VOC limited region. What you see here is, you might…. Suppose you are in this region, as you might be having same NO_2, but suppose your VOC emissions are large, you will make more and more of ozone. That you can see for yourself. You have this level of VOC. Suppose NO_2 or NO_x is increased, what happens to ozone? You have this level of VOC, for example, and then you are in this region, and then after sometime you had more of the NO_x emissions. What might happen to ozone? Decrease. It is not as simple as to say that the NO_x emission will always increase the ozone concentration; it can decrease, but then you should be able to explain it with the science that you know. Here is the VOC limited region. Even in this region, particularly, you will see it is very low. So, most of the NO_2, most of the ozone formation, is governed by the NO_2 that you have. NO is not being oxidized to NO_2, because to oxidize to NO2 either it is ozone or the hydro carsbons. There is no hydro carbons, because very low concentration - 2 pvb. You form the low this thing. As you go here you have the more and more hydrocarbons and high levels of NO_x as well [continuously from here].

Here you have the NO_x limited region. You have to have NO_x. If you do not have NO_x you can never make ozone; is it not? No matter how much increase in VOC you are causing, do you see any change in ozone? It is stable; it is almost parallel to the x-axis. The shape also you see this is the high slope here and almost low slope here can also be explained by this model, also both practical as well as theory. You can see the difference. Increasing the VOC in this region does not cause any problem with ozone. Suppose you already have high NO_X it can cause serious problems. Of course you are in the middle region, if both are high or both are at moderate level, then you can have it. So you can [ ] out this one.

You can very well design your strategy for the control of the ozone. If you want to control NO_x, you want to control VOC(s). Were are you as far as your region is concerned? You might be here - well solutions will be different. If you are here, the solutions can be different. That is also explained by the science. I will pass on more information to you on this one. That also accounts for the formation of NO_x disappearing and things like that. The interesting thing in science you have been able to translate into the models; this is the maximum concentration. This is how we get it.

You should also understand that when it comes to the VOC emissions, they also come from natural sources. That is what again and again we refer [V Kant Patel] we were talking - many of the VOC emissions were from the trees. Not only this emissions that we have, but also VOC emissions can also be from the natural origin or from the plants or what ever that source may be.

As a result, we may form more ozone; we may say there is nothing here, but the ozone levels are high; one of the reasons can be that you have the natural source. When it comes to the pollution control, the management of this thing, then you have to look into many aspects. As far as this thing is concerned, I will give you more information about EKMA and we will do also one example, may be in the next class.

Having said all these things - what is the primary reason, if I ask you, of this air pollution and the emissions what you see in the atmosphere or the air pollution you see - what is the primary reason - if you have to take one important thing. Combustion. It is the combustion that creates 90 percent of the air pollution problem. If you have understood the combustion very well, again it comes to the science, then things can help a great deal.

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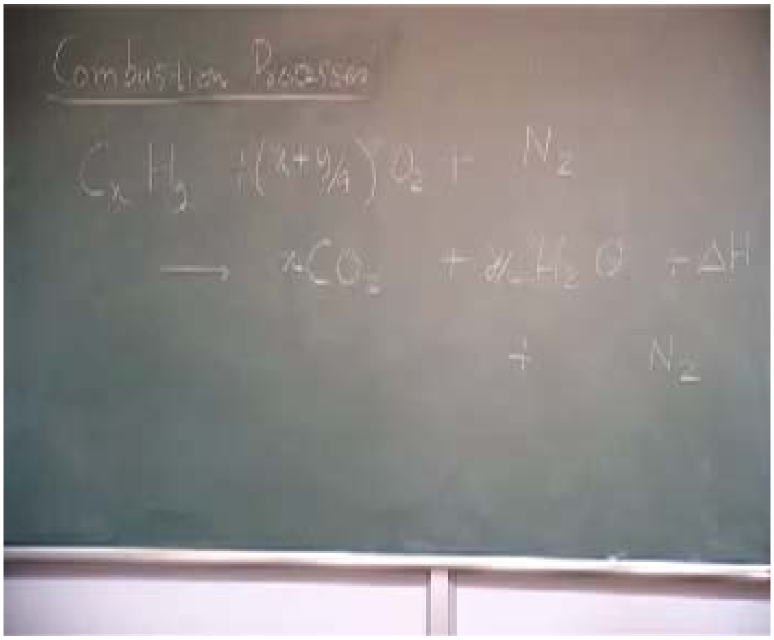

I want to start leave beside the atmospheric chemistry is the combustion processes, because, we want a answer about the source now. Let us say we all know we have to burn the hydrocarbons and then why the combustion? Because we all are crazy after energy. Energy is a big thing. If we do not need energy, then we will not burn so many things. But always energy is required. We want to move something here, we want building construction – energy is required. You want to travel, you want electricity – every where combustion is required. If you need the energy, then the combustion is required. Most of the time what we are firing really is C and H - carbon and hydrogen. Let us make it generalized. Then you are firing it with the oxygen. What you form is if everything goes well, is CO_2. We have to balance this equation, because, that is now getting into combustion; seriously getting in combustion. Hydrogen is y. I have 2y. So what if I say y_2? What is not satisfied now? Please tell me. [Conversation between student and professor – Not Audible (44:04 min)] Let us make it then, simple thing; this makes things interesting and you will remember them. Let us make it small x. It is much easier to write. x plus y by 4. This is not the complete thing. What else I should write? Broadly speaking, not like some small species anything like that. Energy created plus energy, that is fine, is finding delta H; what else?

This is the reason that as to what we were discussing. You will always remember that - what else? That is why I want that answer to come from you. Can I put oxygen alone for the combustion? Can I put just the oxygen; take out the oxygen from the air and separate it out and put it? The whole air has to go in for the combustion. So along with oxygen what will go is the N_2. That might come out as such. [Let us not forget that.] Reaction - I am sure it is balanced, but is there anything we can write little bit in better way than this? [Conversation between student and professor – Not Audible (46:17 min)] You have to consider the O_2 and Nitrogen ratio and probably put that same number here and same number here. Then you are doing a complete job. Although it is balanced of course, but then you have to put the same molar ratio, the amount of the oxygen that you are taking in for stoichiometry the corresponding amount of NO_2 will enter your system. It is good idea to write that number here and here; that really makes this thing complete. The molar ratio of …what is that? Yes, we all can do that one. Tell me - the volume ratio, will it be same as a molar ratio or not? It has to be right Whatever is the volume ratio nitrogen to oxygen same will be the molar ratio.

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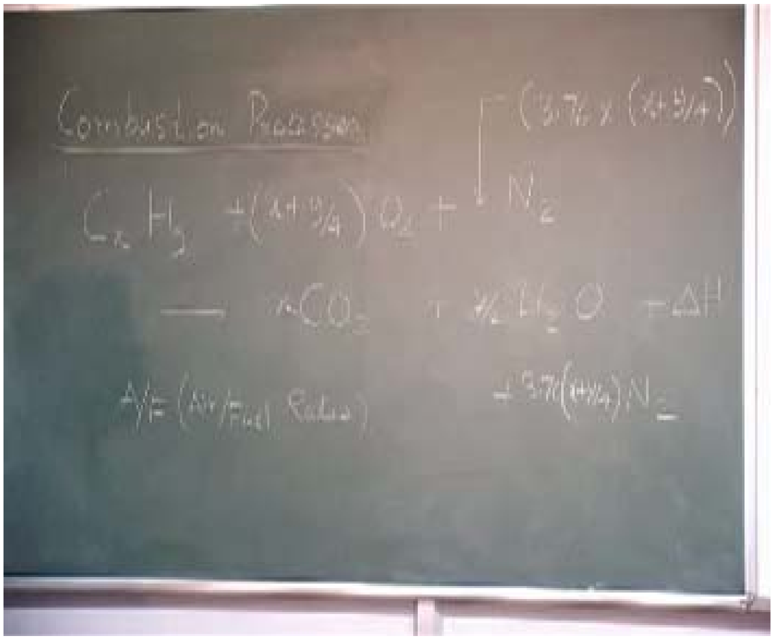

So what can I do here? Let me write it here. I will put here 3.76 times this number (Refer Slide Time: 47:47 min). Same thing here: 3.76 x plus y by 4; that is the complete reaction that we have written.

The other thing which is important in the air pollution or the combustion rather, is something what we call as air to fuel ratio. Generally, it is taken in mass. I can find out the mass of air that is going into it, and mass of the fuel that is going into it, and mass to air to fuel ratio. If this air to fuel ratio - well if you are a mechanical engineer the things look very trivial and you say – that was what I am talking about. Then there are many people who are not mechanical engineers or might have forgotten if it is greater than I write here observed is greater than air to fuel ratio stoichiometry, this system is it called lean or rich (in terms of fuel, of course)?. If I observed air to fuel ratio in the process where I am doing the combustion is higher than the air to fuel ratio as per the stoichiometry which you get from this important reaction that we have written, then this thing will be internal fuel, this air to fuel ratio is lean or have I said the other way? No, this is a lean mixture. If I say A by F observed is less than A by F stoichio this mixture is rich mixture. We have to deal with the rich mixture.

We want to stop it here because this if you go by that watch we have to stop there, but tell me - which situation will be little better for me: lean or rich mixture? What will happen if I go with the rich mixture? The combustion will be incomplete; I will push out many of the hydrocarbons from where I can get the energy and my CO emissions will be larger, because, that CO will not be converted into it.

If you have the lean mixture it will be little better; at least, I am giving it full opportunity to react with oxygen, because, I am putting lot of excess oxygen because higher to air to fuel ratio which means do not forget this really means excess of oxygen and here less oxygen. It does not mean that I can keep on putting oxygen hoping the things will happen, because, you may dilute the things so much that it may not catch fire. Here it probably will catch fire but lot of combustion products will go out. Most of the combustion processes we will have the excess oxygen than what is required; you have to make sure that they complete burning of the fuel.

We will do an example on this one in next class and also talk little bit more stuff related to combustion.