# Environmental Air Pollution

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## Lecture 7
## Atmospheric Formation of Air Pollutants – 1

We did not cover a small portion on particulate formation last time. You can still go back to slide source; I am sure we will load it by today; then you can have a look. I want to quickly move on to something else, that is about the atmospheric chemistry. You remember we have three things: S, T and R – source, transport and receptor. We will be working back and forth; we want to quickly go into atmospheric reaction to see pollutants that are in the atmosphere and what they can do. Can they do good things, can they do the bad things or they may not do anything. We are talking more of the chemical transformation of the pollutants and that depends on many things, but we try to go as much as we need to go.

Atmospheric chemistry can be a big subject in itself, but we will not go that far because we like to cover something in two to three lectures. When we look at the atmospheric chemistry and what is important is that again it can affect the people; it can disrupt the receptor and then it can, in fact, sometimes in the positive sense because atmospheric chemistry cannot only create problems and serious problems, it can also sometimes reduce problems; because, they are able to scavenge out the pollutants, scavenge out the harmful things and can produce something very benign or not so harmful. So there can be positive effects.

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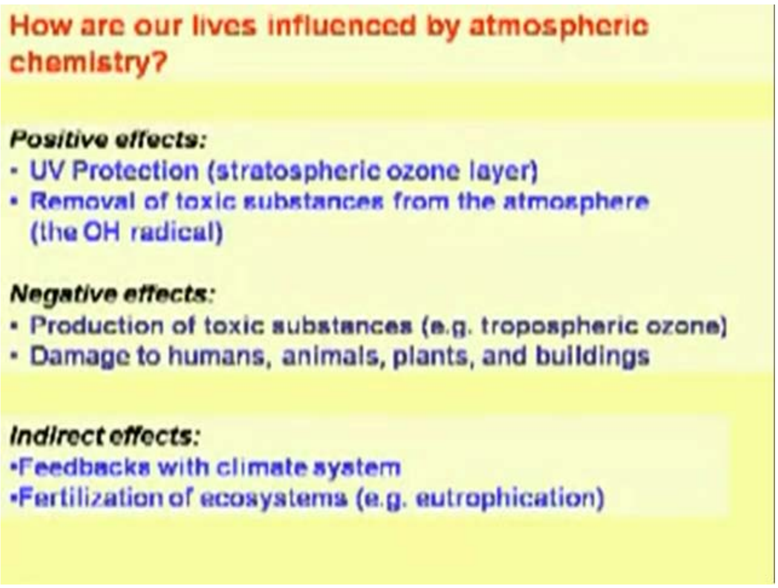

How are our lives influenced by atmospheric chemistry?

**Positive effects:**
- UV Protection (stratospheric ozone layer)
- Removal of toxic substances from the atmosphere (the OH radical)

**Negative effects:**
- Production of toxic substances (e.g. tropospheric ozone)
- Damage to humans, animals, plants, and buildings

**Indirect effects:**
- Feedbacks with climate system
- Fertilization of ecosystems (e.g. eutrophication)

Firstly, it affects the stratospheric ozone, which is being formed in the stratosphere all the time and that is a good thing. It can also remove some of the toxic substances from the atmosphere; for example: the OH radicals and the other things.

The negative effect is that they can produce the substance which is sometimes more harmful, deadlier and more problematic. For example: ozone; as I said all the time when you talk about the troposphere, ozone is a pollutant. Ozone should not be there; because, we do not need ozone in troposphere, but it is formed; none of the processes, generally by and large 99 percent processes do not release any ozone, but ozone is formed. Where? In the atmosphere and in the troposphere that becomes a problem. This is a worldwide problem. In fact lots of efforts are on to measure and to be able to map the ozone load through the satellite and NASA is trying very hard to isolate the pollutant, the areas where more ozone is formed and things like that; because, ozone can damage human, animal, plants and buildings; not necessarily the building, but in some sense, you know, indirectly it can help produce assets which can destroy the buildings.

Indirect effects - the climate change system; we know it is affecting the climate, where the particles can affect the climate; the gases can affect the climate. For example: methane; we all know the effect of methane in terms of the green house gases.

We can also know that some of the particles are formed in the atmosphere that we saw how they view volatile organic carbon compounds; you know like because of the vapour pressure is high, supersaturated. In fact some of the atmospheric reaction can also form the particles not only the through the organic root, we can also form the particles from the inorganic roots. That is why sometimes we wonder that while we are controlling lots of pollution at the source of the particulate matter, we are cleaning the chimneys, but still we find the particles to be there and those particles are formed in the atmosphere from the precursor gases. We control the particle; we are very happy when the chimney looks fine; we have controlled it, but when we go and measure outside, we still get the particles that had originated or that had not originated, but they were formed in the atmosphere from the gases; those gases had originated from the source. So that is a little thing. So unless we understand this mechanism, the science, the chemistry, we cannot manage air pollution.

There are indirect effects also. Sometimes nitrogen can also be down washed and it can affect the even the ecosystem and can add to eutrophication. With this background, let us get to something more serious.

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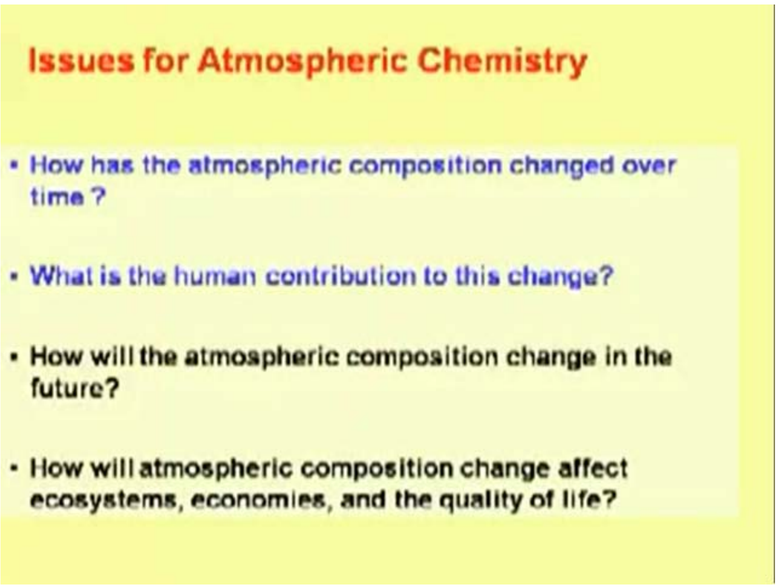

Issues for Atmospheric Chemistry

- How has the atmospheric composition changed over time ?
- What is the human contribution to this change?
- How will the atmospheric composition change in the future?
- How will atmospheric composition change affect ecosystems, economies, and the quality of life?

These are the issues we should be able to answer once we know the chemistry: How the atmospheric composition has changed over time? What is the human contribution to this change? Because, something occurring naturally, a little we can do about that; because, this, the sizes of nature's operation sometimes can be very large; we have no control. For example: some things are changing because of the volcanic activities. What can we do? Nothing. We cannot go and stop volcano; but something what we do, we can certainly control that and we should try to control that because the natural sources can also be interesting. Some of you remember the presentation by Dr. Ravi Kant Patak? He tells you how the trees can pollute in terms of the organic vapours and organic things that can come out. Remember, he also said those vapours present, in presence of seeds, like ammonium nitrate, sulphate would produce more particulate; you recall that? So nature can also play and sometimes to handle nature could be difficult.

What is the human contribution? How will the atmospheric composition change in future? How the atmospheric composition changes effects the ecosystem, economies and the quality of life? That can be another thing, but we will stay more or less with the science, but the implication of science is essentially to answer the questions that are being raised here.

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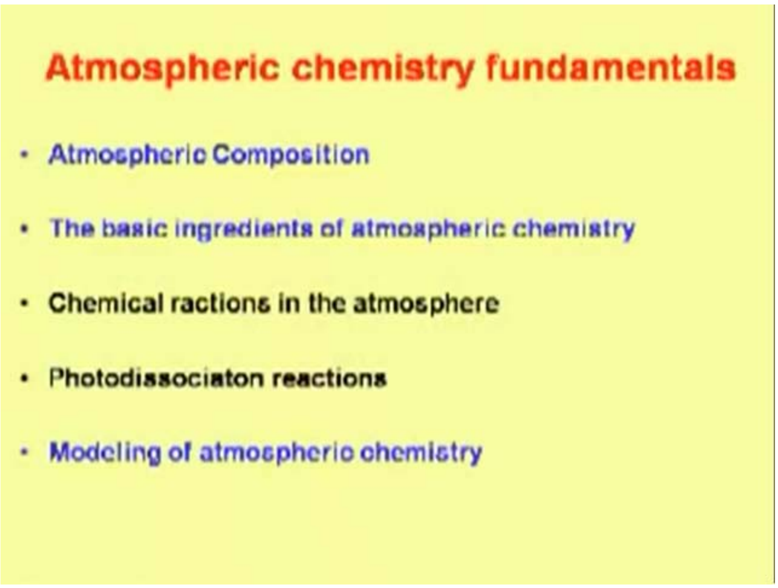

## Atmospheric chemistry fundamentals

- Atmospheric Composition
- The basic ingredients of atmospheric chemistry
- Chemical ractions in the atmosphere
- Photodissociaton reactions
- Modeling of atmospheric chemistry

Atmospheric chemistry fundamentals: we know about the atmospheric composition, the basic ingredients of atmospheric chemistry; it is very important to understand as to what happens with chemical reaction in the atmosphere. We have to understand chemical reaction kinetics, you have to understand the conditions under which things can happen, temperature is very fundamental to many of the reactions. The temperature is important, the humidity is important and above all these things, what do you think is important?

Where is all energy that will come from to break and you know we need energy all the time and then energy comes from the sun. The sun will bring a lot of energy. We will talk a lot about the sun's energy that is coming in; in fact, the atmosphere in terms of the pollutants could look very different in the day and the night it could to be different. On a day when it is very heavily over cast, you are not getting enough of the sun and you may find the atmosphere looks very different. Thus, if you have the knowledge, if you have the science with you, then you can explain these numbers. So that is what you see, is very important to understand the science.

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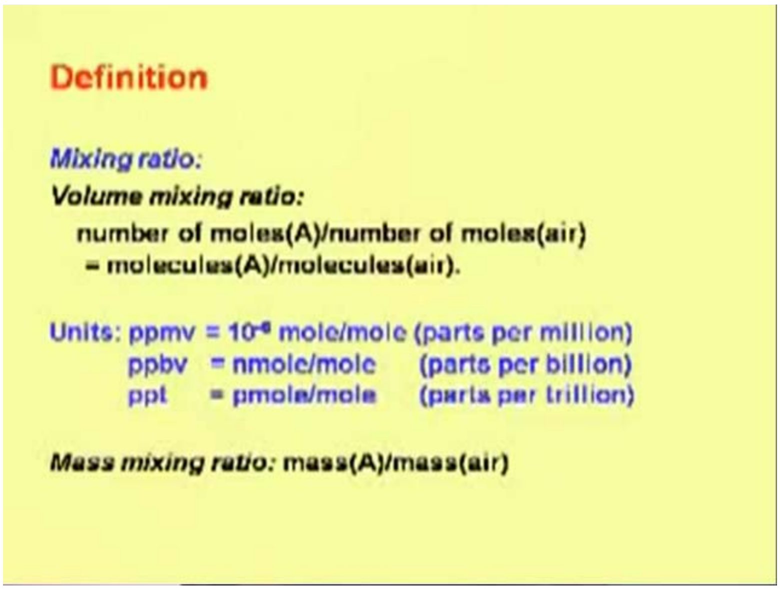

**Definition**

*Mixing ratio:*

***Volume mixing ratio:***

number of moles(A)/number of moles(air)
= molecules(A)/molecules(air).

Units: ppmv = $10^{-6}$ mole/mole (parts per million)
ppbv = nmole/mole (parts per billion)
ppt = pmole/mole (parts per trillion)

***Mass mixing ratio:*** mass(A)/mass(air)

We did this last time. We tried to define ppm by volume; that is, 10 to the power minus 6 mole per mole of the gas versus air. The ppb will be you know the nano moles per mole and this is the peaker moles per mole; that will be the ppt, that is parts per trillion. That we have done last time; so we will quickly skip this and go on to something else. Now, these are the things we shall talk. Let me again tell you things are far more complicated and the number of reactions that happen in the atmosphere can run into thousands.

Some people, who try to understand the system want to model it; because, see why we model the things, because it is impossible for us to measure everything; it is impossible for us to have such a system that can measure everything. Whereas, if you can model it, you can model everything as function or time, how the things are changing: What will happen at nine o'clock? What will happen at fifteen minutes past nine? And what will happen at five in the evening? So we can model it. Basic things, which are the important things that we will discuss in this course, at some point or other these are things that we will discuss.

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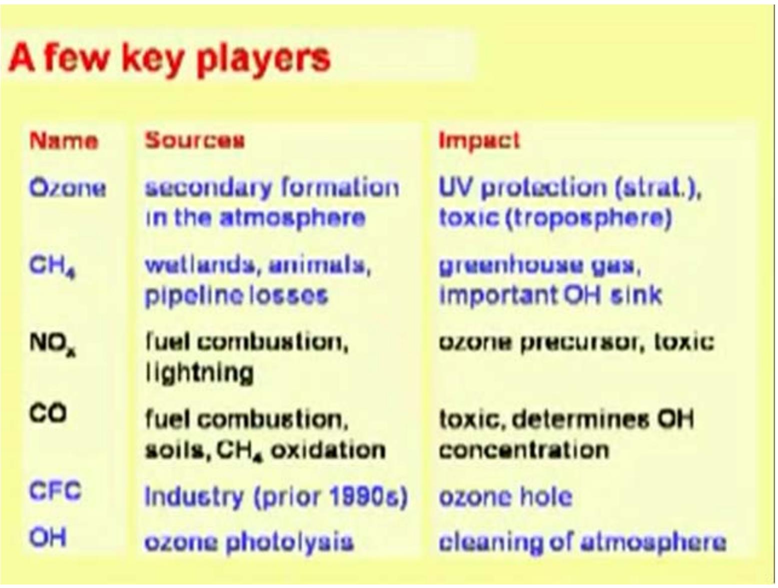

## A few key players

| Name | Sources | Impact |
|---|---|---|
| Ozone | secondary formation in the atmosphere | UV protection (strat.), toxic (troposphere) |
| $CH_4$ | wetlands, animals, pipeline losses | greenhouse gas, important OH sink |
| $NO_x$ | fuel combustion, lightning | ozone precursor, toxic |
| CO | fuel combustion, soils, $CH_4$ oxidation | toxic, determines OH concentration |
| CFC | Industry (prior 1990s) | ozone hole |
| OH | ozone photolysis | cleaning of atmosphere |

Ozone, we understand sources; as I have been repeating again and again in troposphere, ozone is always a secondary pollutant. Ozone is not created, generated from the primary sources. You will not find ozone by and large from any chimney exhaust; it is just formed in the atmosphere. Who is the main player or the impacted? UV of course. This is UV protection, but then for the ozone formation again what is important is UV. That we will see probably today in class.

We also have methane emission. Generally methane is not emitted by our industrial processes by and large not so much, but then we have the wetlands, we have animals and their waste - that will produce the methane constantly through the bio degradation; you all know about that. Methane is a very serious greenhouse gas. How many times more potential than $CO_2$? 16 times; that is correct; 16 times as higher potential than $CO_2$. What is the pipeline indicating? See the methane is the gas which is transported – CNG; so there could be leakages right. CNG is a big way now and the methane is transported from lots of places, from one end to another one; so there could be leakages that are the pipe losses.

We also have the $NO_X$ problem that I discussed with you. Again, let us quickly recap. What is $NO_X$? NO plus $NO_2$. What is largely at the emission source? NO. What is largely in the atmosphere, what do we breathe? $NO_2$.

We also have the CO that that is formed, that is toxic. You will see again and again OH appearing here. So, we should see that how OH will play a very significant role of course.

Again, it is not as a thing that is emitted from the source. It is formed in the atmosphere and it is, we all know, even from our water chemistry, OH is hugely reactive. Its concentrations are very low actually. Sometimes, you will wonder what are the units in which we normally measure the OH. Moles per litre? Its concentration is very low .00000 or something. Interestingly, sometimes it can be measured in number of molecules, for example, 10 to the power of 12 molecules per litre. That is low concentration, but the role which it plays is very vital.

We all know about the CFC business and then ozone photolysis. In fact, some ozone is formed and then the OH is again formed from the ozone synthesis. This can also clean the atmosphere. These are the positive things; that will become clearer to you.

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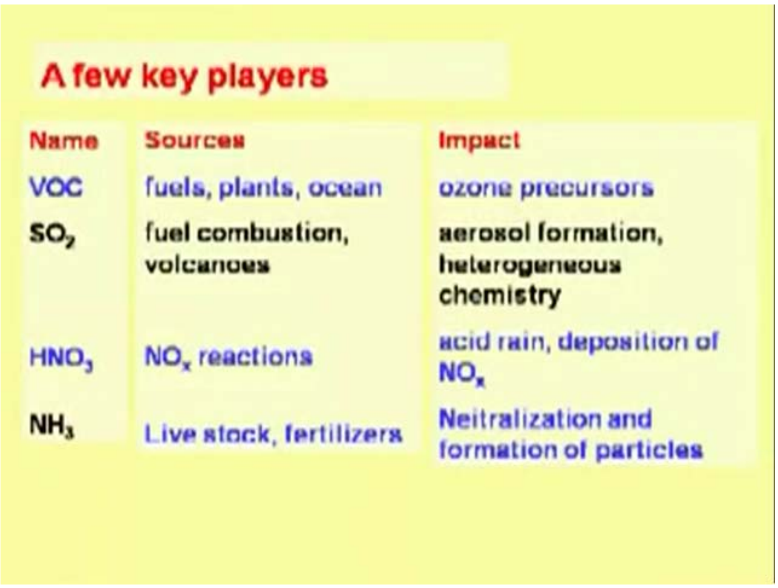

## A few key players

| Name | Sources | Impact |
|---|---|---|
| VOC | fuels, plants, ocean | ozone precursors |
| $SO_2$ | fuel combustion,<br>volcanoes | aerosol formation,<br>heterogeneous chemistry |
| $HNO_3$ | $NO_x$ reactions | acid rain, deposition of $NO_x$ |
| $NH_3$ | Live stock, fertilizers | Neitralization and formation of particles |

VOC is volatile organic compounds. Sources fuel this thing and then it is very funny that you see here, that this can also lead to formation of ozone; we will see it sounds very funny but then it can also lead to form the ozone. $SO_2$ again fuel combustion, volcanoes, aerosol formation and heterogeneous chemistry. This can also lead to acid rain; the impact of $SO_2$. The interesting part is that $SO_2$ can also be responsible for aerosol formation. So if you want to control aerosol, you not only need to control the aerosol at the source but you may need to control $SO_2$ as well. So, $SO_2$ control will not be determined by the $SO_2$ concentration in the ambient air for the people to breathe; $SO_2$ concentration may be in the emission, may be controlled or regulated by the particulates that we need there. So look at the complexity of the thing and some other things we will learn. $NO_X$ similarly, almost the sole source of $HNO_3$ in the atmosphere is from the $NO_X$ reaction. Some of the $HNO_3$ is released from the nitric acid plants also, but that is not so. This thing will be a very local phenomenon.

Ammonia is very interesting pollutant. It comes from the livestock. How does it come from the livestock? It comes from waste degradation. The fertilizers, the amount of urea used, some of the ammonia can escape from there. The interesting part about ammonia is that they can neutralise both $HNO_3$ and sulphuric acid, but they also add to the formation of particle. How? What will $H_2SO_4$ and ammonia form? It will form ammonium sulphate and ammonium sulphate are the particles. $H_2SO_4$was in the vapour phase or in the mist form; this was in the gaseous phase and what you got in the atmosphere as a result is particulate pollution. That is a little tricky there – the ammonia issue. So this will give you the idea and let us get into the chemistry now.

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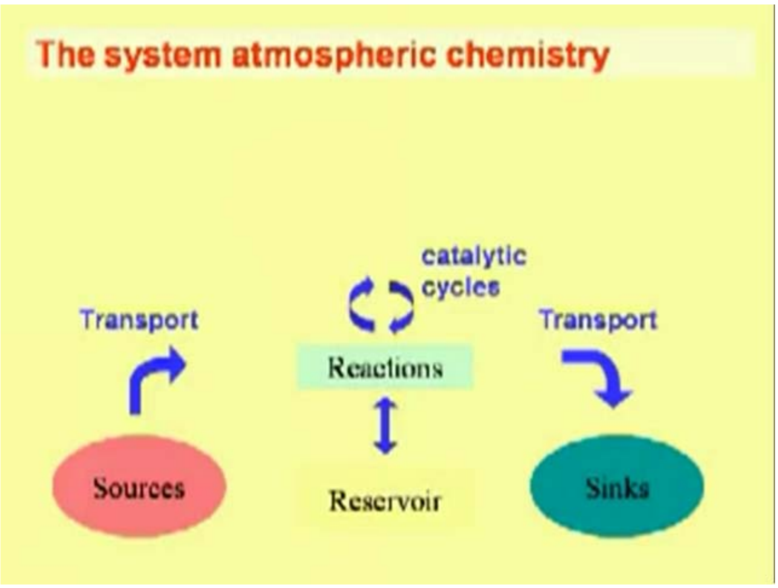

The system atmospheric chemistry

This is something we all know. I have talked about this: the source, transport, reaction transport and then there has to be sinks. Sink is how the things get out of the system. If there were no sinks, these pollutant levels and the secondary pollutant will continue to rise. Then the survival of the people and the things will completely stop; so it is very important to understand the sinks. So let us get into some more specific things, that is atmospheric and also the catalysts.Did I gave you example of how $SO_2$ was transformed to $H_2 SO_4$?

Does anyone remember how sulphuric acid is produced in the sulphuric acid plant? It does not matter if you do not remember. What we do is we take the sulphur, burn it, make sulphur dioxide, then oxidise $SO_2$ to $SO_3$. How do you oxidise $SO_2$ to $SO_3$? It is a catalytic oxidation of $SO_2$ to $SO_3$; conversion of $SO_2$ to $SO_3$ is not easy.

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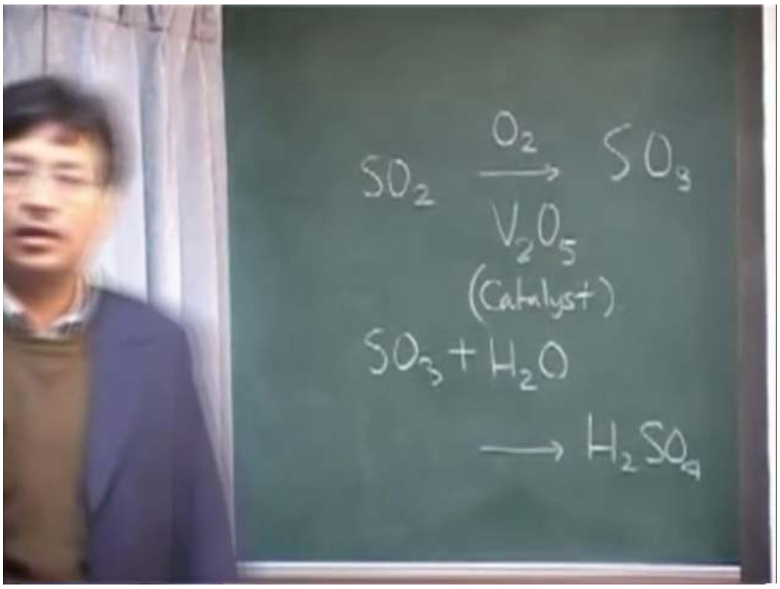

So in the sulphuric acid plant, once you are producing $SO_2$, you supply oxygen, no doubt about it, but provide a catalyst. I do not know now if you can recall that vanadium pentoxide is a catalyst to oxidise $SO_2$ to $SO_3$. You need to balance this, of course, which you can do; then, once you have this $SO_3$, this $SO_3$ is reacted with water or absorbed in the water and you get $H_2SO_4$; this is what I mean as a catalyst. Almost identical reactions can occur in the atmosphere; you have the $SO_{2,}$ the level shall be extremely low. Here you may also have the catalyst present in the atmosphere that is vanadium pentoxide. Where does the vanadium come from? There could be many sources, but almost all comes from diesel or fuel oil it contain vanadium; these contain a bit of vanadium because it is extracted from the ground. The vanadium goes in the air; I do not know what the atomic weight of a molecule of vanadium is, any idea? It is pretty heavy. So when you do the distillation, the vanadium continues to be at the lower end; it does not go out and does not appear. So in the fuel oil or the furnace oil, the vanadium will be there. It will find the source in the atmosphere $SO_2$ and it can form the sulphuric acid. This is one of the routes; there are many other ways

So the catalysts play important role and our atmosphere is oxidizing in nature because we have lots of oxygen there. What else? The role of the catalyst cannot be undermined and that is what is being seen. I just gave you a little example for how sulphuric acid could be formed; there are other ways also that it could be formed; the one important thing is oxidation to $SO_3$, then to react with water and this reaction is almost an instantaneous one. $SO_3$ is more or less unstable and it quickly wants to react.

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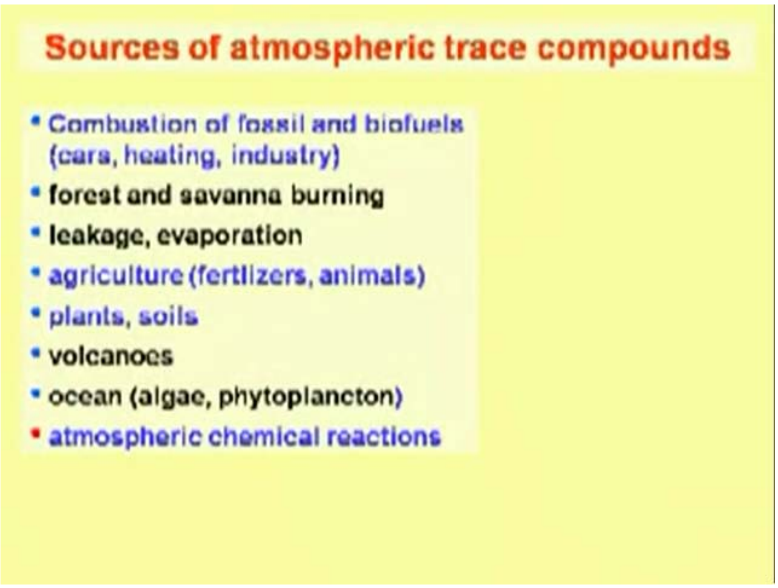

## Sources of atmospheric trace compounds

- Combustion of fossil and biofuels (cars, heating, industry)
- forest and savanna burning
- leakage, evaporation
- agriculture (fertlizers, animals)
- plants, soils
- volcanoes
- ocean (algae, phytoplancton)
- atmospheric chemical reactions

Now this slide, we do not want to keep for long, you know about this. There is combustion of the fossil fuel and bio fuels, cars, heating, industry, forest and this savannah burning. You see there are lot of work on the natural forest fire and that also produces lot of trace compounds. Leakage and evaporation we have discussed. Agriculture; sometimes you wonder why agriculture can be a serious source of emissions of not only the dust that comes from the tractor and the people working, but they are also spreading the urea. So ammonia comes out; you are spreading the pesticide and many of the pesticides are volatile and they are heavily spreading it. Things can be volatile and you are putting it onto the field and then it can just become volatile. It can again make the particulate or it can stay in volatile phase.

This is the latest thing people are talking a great deal about - the air emissions and the air pollution from the agriculture activities. Plants and soil can also sometime give out pollutants and so can volcanoes and oceans. In atmospheric chemical reactions we get trace compounds.

Let us see some of the major issues. Let us first quickly recap the chemistry part. You have done it all; you will have a simple reaction to recap the things. You all know where the reactions can happen between two compounds; these things, the more reversible thing you can write it in this form and then what is M? [Conversation between Student and Professor – Not Audible (21:01 min)] That is one part, what else can it be?

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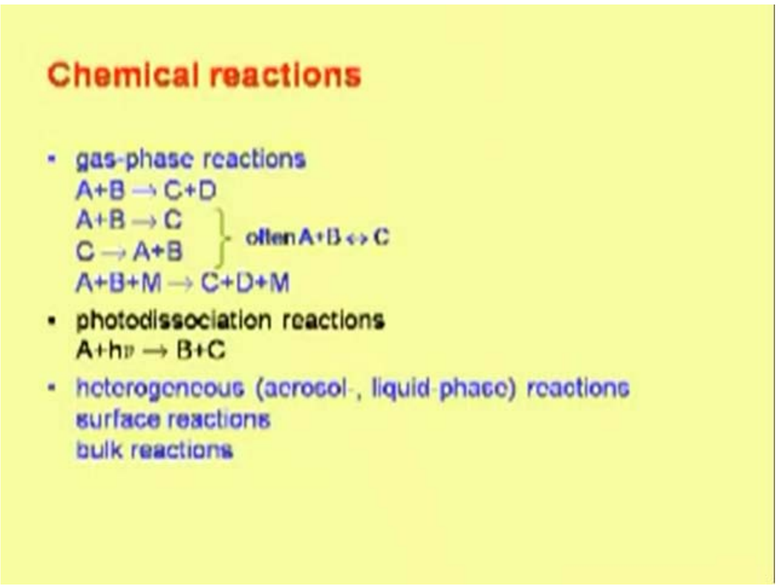

### Chemical reactions

- gas-phase reactions
  $A+B \rightarrow C+D$
  $A+B \rightarrow C$
  $C \rightarrow A+B$
  often $A+B \leftrightarrow C$
  $A+B+M \rightarrow C+D+M$
- photodissociation reactions
  $A+h\nu \rightarrow B+C$
- heterogeneous (aerosol-, liquid-phase) reactions
  surface reactions
  bulk reactions

What happens when you are having some reactions, a lot of energy that is created, vibrational energy, the temperature energy, so something should be there to absorb that energy. That part is generally largely done by nitrogen and oxygen. So we should not forget that some energy comes out. Suppose, let me tell you for example, if the reaction was a plus b equals to c plus d plus heat. Let us talk about that.

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Reversible reaction c plus d plus heat, for example, this thing can happen. Most of the reactions are oxidising in nature. So what will happen if the heat is there? What happens if I do not remove the heat? What can happen? Reverse reaction, yes. So, c plus d is being formed. Then suppose there is no one to take care of the heat, it might just go back. So what we are assuming is that for this reaction which might happen sometime, you also can have this is one of kind of energy; there can be another kind of energy which can be there; so there should be someone to absorb the energy or it can be catalysed as well. There will be some chemicals, some gas, something that can absorb, for example: nitrogen, oxygen largely; that does not change so much in composition but they are able to absorb the energy. Somebody tell me: what is the difference between homogeneous and heterogeneous reactions?

[Conversation between Student and Professor – Not Audible (22:56 min)]

Same phase - that is the key word. So gas versus gas is a homogeneous reaction. Liquid versus liquid is homogeneous. Solid versus solid is homogeneous and then the heterogeneous. So we should all understand that there could be different kinds and then it could be heterogeneous, it could be surface reactions, it could be the bulk reaction, where the things are mashing into another one and the reactions can happen. There is little, what you will recall, that you have done in high school but still we need to have a look on to this one.

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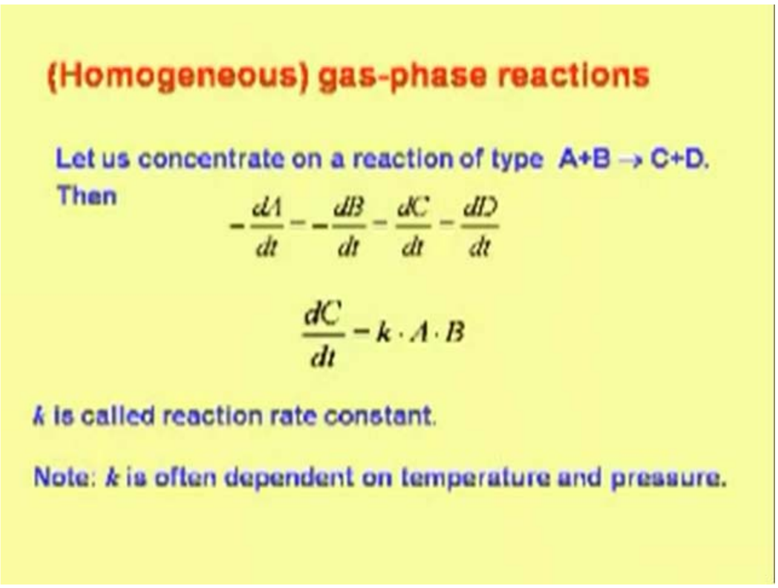

(Homogeneous) gas-phase reactions

Let us concentrate on a reaction of type A+B → C+D.

Then

$$-\frac{dA}{dt} = -\frac{dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt}$$

$$\frac{dC}{dt} = k \cdot A \cdot B$$

*k* is called reaction rate constant.

Note: *k* is often dependent on temperature and pressure.

Think of the reaction - a plus b plus c plus d; then I can write the rate of change of the concentrations of the compound with time and fortunately here, all coefficients are 1. So you can write the rate of change will be da, will be equal, or decrease in da will be equal to decrease in dv and that will be equal to increase in dc. Then you can have dc and dt is one which will be on the plus side as you can see. Let me use this concept and then also this reactions and the real concentrations of a, b, c and d will depend on largely on the recall rate constant, [ constant] and that sort of thing; you all know about that.

What if the coefficient was not 1? Here the coefficient is 1; a - 1, b - 1, c - 1, d -1. But how do you write that? I am just talking about this one only; I am not talking about the final concentration; I am talking about the rate of change of a, b, c, d. 1 by a da dt equals to 1 by d minus, of course dv dt equals to 1 by c dc dt 1 by dd dt. So do not forget that. So what you have done before, in general, I am saying the change in the c will depend on how much is the quantity I have in terms of a and b times rate constant. You all know about that.

K is called the reaction rate constant or rate constant. K often depends on the temperature and the pressure. What are the units of k? Absolutely; order of the reaction and so it is not pressure; that was the reason I asked you. These are little fundamentals but we need to be very clear about these things. We will utilise this very quickly as we go by. So we will apply some of these concepts.

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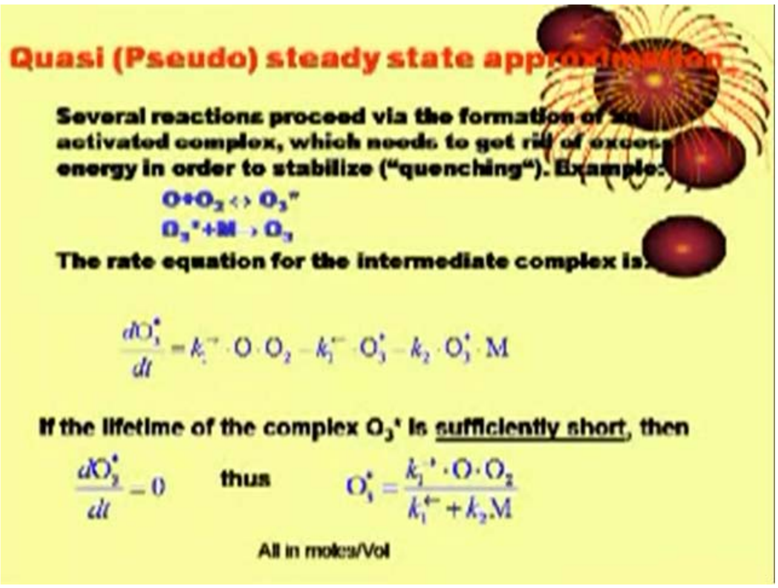

Quasi (Pseudo) steady state approximation

Several reactions proceed via the formation of an activated complex, which needs to get rid of excess energy in order to stabilize ("quenching"). Example:

$O + O_2 \leftrightarrow O_3^*$

$O_3^* + M \rightarrow O_3$

The rate equation for the intermediate complex is:

$$\frac{dO_3^*}{dt} = k_1^{\rightarrow} \cdot O \cdot O_2 - k_1^{\leftarrow} \cdot O_3^* - k_2 \cdot O_3^* \cdot M$$

If the lifetime of the complex $O_3^*$ is sufficiently short, then

$$\frac{dO_3^*}{dt} = 0 \quad \text{thus} \quad O_3^* = \frac{k_1^{\rightarrow} \cdot O \cdot O_2}{k_1^{\leftarrow} + k_2 M}$$

All in moles/Vol

We also need to understand little bit about the quasi or pseudo steady state situation. That will become clear to you about this steady state. For example, several reactions proceed via the formation of an activated complex and that decides what is going to happen. We shall need to get rid of the excess energy in order to stabilise or quenching of this one. For example, O plus $O_2$, you have nascent oxygen. It can form ozone in the excited state. It must shred off the energy to someone to become at the ground state. The rate of equation for the intermediate complexes is given by, and now you see here, what I am trying to write is the rate of change of concentration of $O_3$ in the excited state.

So we have to see in what way $O_3$ is formed, which reaction is forming $O_3$ in the excited state? This one or this one? (Refer Slide Time: 27:25 min) The first one; because, this is the product, and here I am destroying it. So write the concentration in terms of the change in the concentration, that is, input minus output, that is the change. This is the input if I am saying $k_1$ o times $O_2$ minus $k_1$ $O_3$.Why this? It is a reversible reaction, that is okay. This can also go this way, fair enough. Plus or minus I do not know, again minus; again this reaction also will destroy. You should learn these little simple things; you need to learn that how you can write these equations. Simple things but it gives you big results. That you can write here.

The lifetime of the complex 3 is sufficiently short; it can be called pseudo study state; it is being formed and is being destroyed. So in that case, if I can take this equals to 0, then I can find out what will be the ozone concentration in the excited state. Does it mean something is being destroyed quickly? If the rate of generation and rate of destruction is the same, does it mean the concentration is 0? No. That is very important. Concentration is time independent or time invariant. Is the statement okay? Concentration is not changing with time but it has concentration. So those things which are quickly destroyed and the same rate they have been produced, the same rate they have been destroyed, is what we take that assumption; that is called as a quasi or pseudo steady state. That is what we apply the concept of pseudo steady state and then you can find out the concentration. We understand the reaction and if you need to know this concentration, with little knowledge of chemistry, we will be able to say what is happening in the atmosphere. Any questions?

Question: Sir, this like concentration and time dependence is this relation is only for short duration reactions?

Answer: For any reaction.

Question: Sir, suppose we take lot of concentration much as time like it could be changing per unit time or like changing increasing or decreasing with time?

Answer: If that is the case your function, you should represent that.

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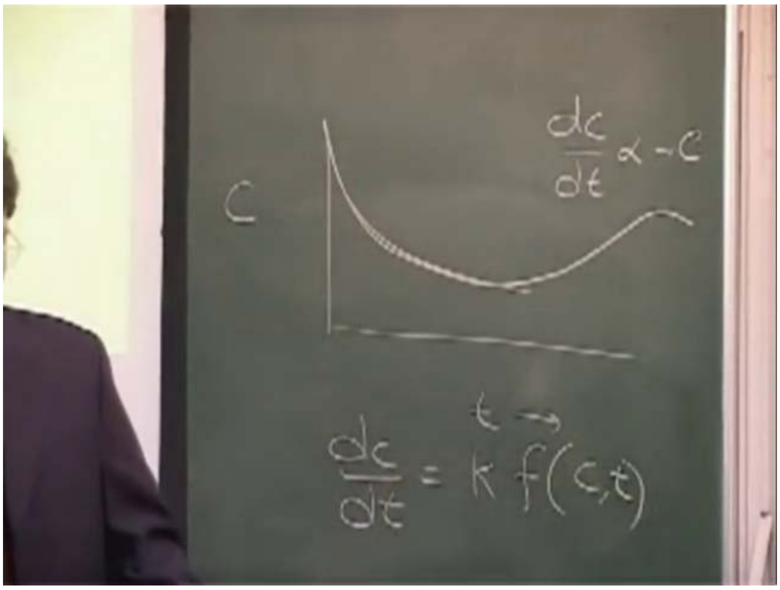

Here t and concentration. Concentration line in mostly water pollution air pollution we say s at state things decrease with first order reactions; so it can go like this.

It is then that you write simply all you know about that. Suppose this was like this, then obviously the dc dt, the function of this curve will be different (Refer Slide Time: 30:49 min). That is all it needs to be. But it may not be very easy to write function, that is a different thing. You should able to write dc by dt is constant and some function of c, ct; that is all you need to write. Do not forget that all we are referring is moles per volume. It is the first time where we are seeing the moles.

There is a little chemistry that we talked about, and let us try and then we go to the real problem, with this back ground. Most of the reactions that we will discuss will be driven by the photodissociation.

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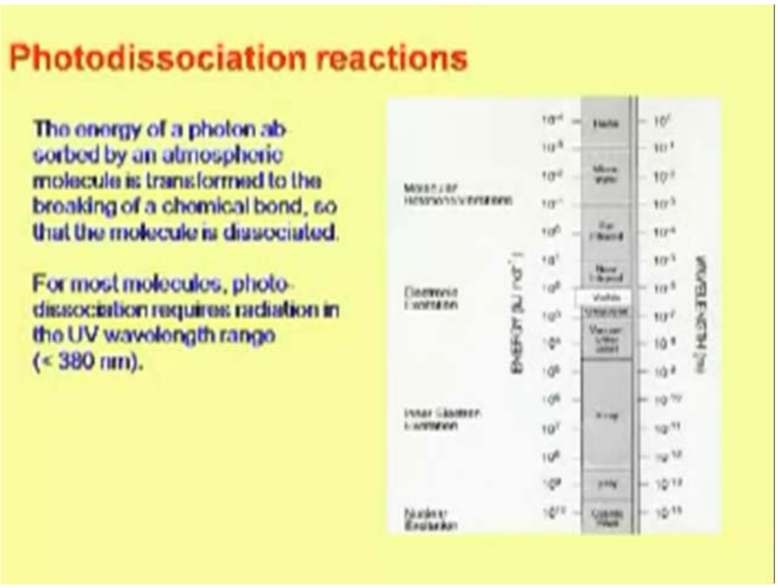

## Photodissociation reactions

The energy of a photon absorbed by an atmospheric molecule is transformed to the breaking of a chemical bond, so that the molecule is dissociated.

For most molecules, photodissociation requires radiation in the UV wavelength range (< 380 nm).

Photo dissociation means you have the UV, that is energy and that is able to break the things; that is in simple terms. The energy of a photon absorbed by an atmosphere molecule is transformed to the breaking of its chemical bond, so that the molecule is dissociated and forms something else. For most molecules photodissociation requires radiation in the UV range that is below 380. Molecule photodissociation requires radiation in the UV range. So the sunlight destroys some UV radiation but some UV radiations still reach us. This will trigger many of the reactions. You all know where the energy issues are there and how the energy and the wave length related? Inversely. And if I have taken down the frequency? What is the constant of proportion? Planks constant.

[Conversation between Student and Professor. Not Clear. Refer Slide Time: 32:44 min)

But what happens is this is where most of our atmospheric photo-oxidation or photodissociation takes place in with the help of this visible range and that too largely less than 380 nanometer.

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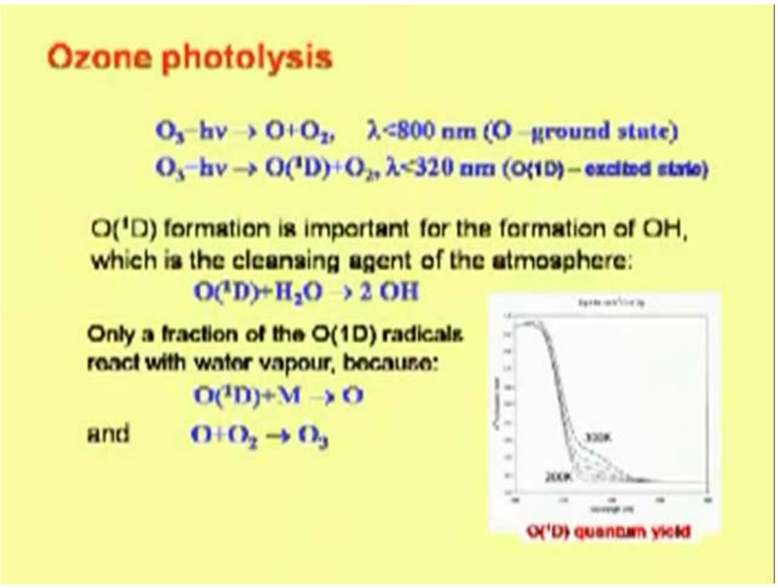

## Ozone photolysis

$O_3 + h\nu \rightarrow O + O_2$, $\lambda < 800$ nm (O – ground state)
$O_3 + h\nu \rightarrow O(^1D) + O_2$, $\lambda < 320$ nm (O(1D) – excited state)

$O(^1D)$ formation is important for the formation of OH, which is the cleansing agent of the atmosphere:

$O(^1D) + H_2O \rightarrow 2\ OH$

Only a fraction of the O(1D) radicals react with water vapour, because:

$O(^1D) + M \rightarrow O$

and $O + O_2 \rightarrow O_3$

$O(^1D)$ quantum yield

We have the time. So let us do this one. For example: if you have ozone, for this, actually you can bring down to O plus $O_2$. It can be broken down by the two different wave lengths and then it can produce O plus $O_2$. This O can be in the ground state and if you have this thing, this O can be in the excited state. So, you see here, if I have shown here, this O is in the ground state, from here you see O and O; this O can react with oxygen to bring back the ozone. But if it is in excited state, because with this nano meter, if it is in excited state, do you see this reaction is reversible or non reversible? It is non reversible. I can never get back ozone from this route. If my energy is coming in this range at this nano meter, you see there once I get this thing I am not going back to ozone; very interesting thing, you have to observe that and keep in mind. Unfortunately, you must understand that you are not getting a great deal in this.

So there must be somebody to react with the excited ozone. Ozone formation is important for the formation of OH radical. You recall, in the beginning of this class, I was emphasising OH and really OH is very important. I am just giving a little idea where the OH is coming from. There are other sources of OH as well. What you see here is that the OH came. It can react with the water vapour in the atmosphere and in the conditions of the humidity, temperature that we get in the atmosphere; so we can get the OH radicals.

Why are the OH radicals high in the atmosphere? In the day time and we have lots of (( )) news. So here you can make the OH radicals, no problem. So quickly tell me: where is the energy more? Here or here? 320. So if energy is more, I am likely to get more OH radicals. It also depends on the temperature. Why? If temperature is more then you have higher this one. Why? Because the energy will be higher for high temperature; body at higher temperature will radiate more in the smaller range, if you recall. You have higher temperatures in the day time and then you will have more $O_1$, the excited atomic oxygen and then you will get and more of OH. Therefore, what I can tell you is chemistry or atmospheric chemistry will be different for us, will be different for America, it will be different for north, for example, Norway, because our temperatures are high and so our radiation, our (( )) will be more and our chemistry will be entirely different. So we need to study the chemistry, and the science and then apply to our local condition.

Always remember science is universal; whereas, the application of science is local or regional. Interesting statement: science is universal; whereas, the application of science is local or regional. So you see here in India, for example, will be very different then what can happen which is very evident because (( )) will be different than what we are getting the energy. So there will be variation between winter and summer. There could be a variation in the monsoon period, when you have lots of overcast conditions.

So, unless we know the science, we will not be able to tell what is happening to ozone; what is happening to the OH radicals.

[Conversation between Student and Professor – Not Audible ( 37:41 min)]

Excited oxygen and the grounds depending on the radiations that you are getting; both routes can happen. The first route: this ground oxygen can react back with oxygen to produce ozone again. When this producing ozone again then it is like kind of a null situation; nothing is happening basically - production, destruction; production destruction. But in the second route, where you have more energy with less than 320 nano meters wave length, it breaks to ozone, which is excited state plus $O_2$ and this excited atomic oxygen and $O_2$ will not react to produce ozone back. So this one become somebody should take on to that who takes on is water is one of the thing the other can also take and that will produce OH radical. In fact, 1 atomic oxygen molecule in excited state will produce 2 molecules of OH.  Any questions? Alright, then let us proceed.

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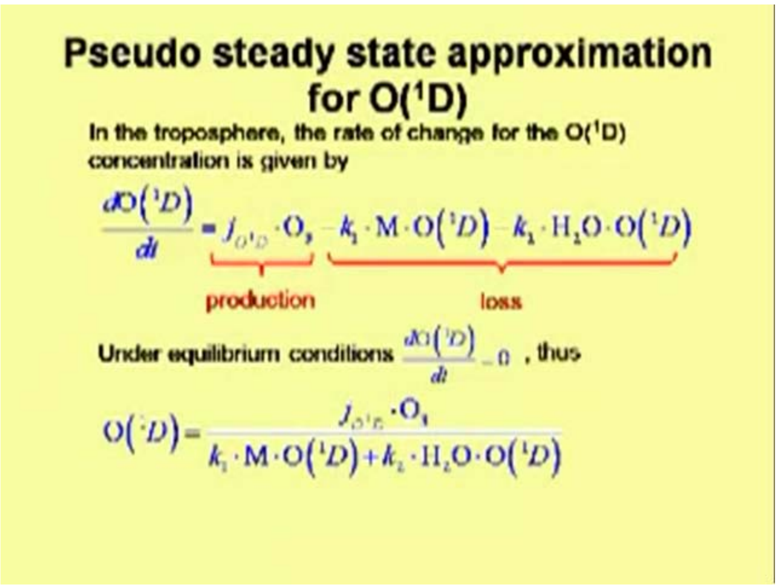

**Pseudo steady state approximation for $O(^1D)$**

In the troposphere, the rate of change for the $O(^1D)$ concentration is given by

$$\frac{dO(^1D)}{dt} = \underbrace{j_{O^1D} \cdot O_3}_{\text{production}} \underbrace{- k_1 \cdot M \cdot O(^1D) - k_2 \cdot H_2O \cdot O(^1D)}_{\text{loss}}$$

Under equilibrium conditions $\frac{dO(^1D)}{dt} = 0$, thus

$$O(^1D) = \frac{j_{O^1D} \cdot O_3}{k_1 \cdot M \cdot O(^1D) + k_2 \cdot H_2O \cdot O(^1D)}$$

We are now talking about pseudo steady state for excited state of O and D. I am not using k, I am writing j, many books use j. Quickly, see from the notes or the earlier figure and make sure that I have written correctly. Just spend about less than 10 seconds and then let us say I have written correctly or may be wrongly.

[Conversation between Student and Professor – Not Audible ( 39:15 min)]

Was there any reaction reversible for $O_1$d? No. So, it can react and produce, react to the water and get destroyed, this $O_1$d. $O_1$d can also be destroyed by this root. So again pseudo steady state is equal to 0. You can even find what will be the concentration of excited atomic oxygen, given the ozone concentration, given this concentration of this and this and sometimes this we take a constant. Then you see that you can find out. This equation will not be so easy to solve because you also have this in here. It is not a simple equation to solve but you can solve this one and then the same.

Now, I want to come to the real atmosphere, that is all for the background part of it. Pay attention. Now the idea of showing this one is now we can go little fast. This is what is happening really in the atmosphere.

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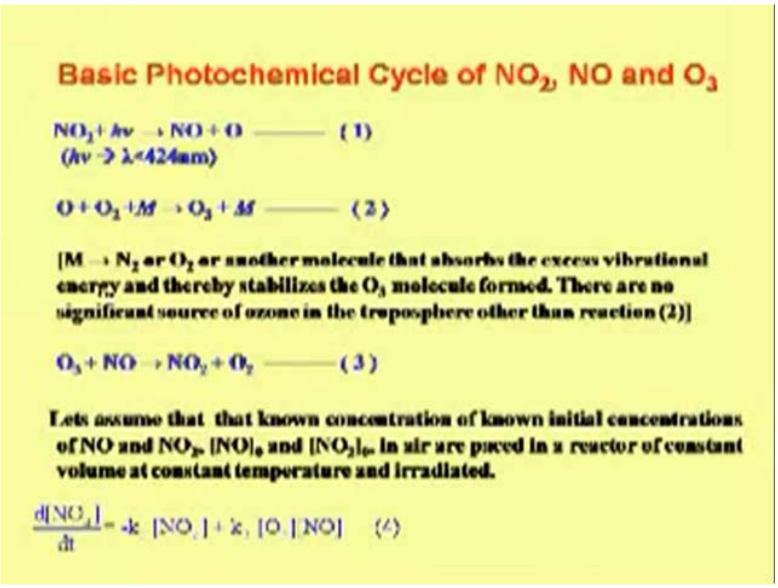

## Basic Photochemical Cycle of $NO_2$, NO and $O_3$

$NO_2 + h\nu \rightarrow NO + O$ ——— (1)
($h\nu \rightarrow \lambda < 424nm$)

$O + O_2 + M \rightarrow O_3 + M$ ——— (2)

[M → $N_2$ or $O_2$ or another molecule that absorbs the excess vibrational energy and thereby stabilizes the $O_3$ molecule formed. There are no significant source of ozone in the troposphere other than reaction (2)]

$O_3 + NO \rightarrow NO_2 + O_2$ ——— (3)

Lets assume that that known concentration of known initial concentrations of NO and $NO_2$, $[NO]_0$ and $[NO_2]_0$, in air are paced in a reactor of constant volume at constant temperature and irradiated.

$$\frac{d[NO_2]}{dt} = -k_1 [NO_2] + k_3 [O_3][NO] \quad (4)$$

We know that we are finding, [ ] lot of $NO_2$ where the $NO_2$ has come. $NO_2$ initially comes from NO. $NO_2$ – it is very photosensitive, more than the most of the compounds. So this is the range which is not filtered by the ozone layer and still reaches the ground; because, ozone layer is not filtering all UV radiation. May be you will recall that it can stop some, but it cannot stop some. So this thing can reach this kind of energy, this kind of O can reach and then this is specifically sensitive to this; then this can be broken down to NO plus O. This O can react with $O_2$ to form ozone. What is this O - tell me: is it is in excited state or it is in ground state? Ground state; then only it can react with $O_2$, if you recall the first thing and then produce ozone. Equations 1 and 2 are the fundamental equations to form the ozone in the atmosphere. We were talking great deal about atmosphere. Do not forget that we are now discussing troposphere. We are not in the stratosphere or the higher atmospheres.

So this is a basic fundamental equation. That is how you constantly get ozone from here. M, which is $N_2$ or $O_2$ or another molecule that absorbs the excess vibrational energy and thereby stabilises the ozone molecule that is formed. There is no significant source of ozone in the troposphere. So by and large whatever ozone is formed in the troposphere is governed by equation 2. I will agree with this one and largely with equation 1; because, almost no other photochemical reaction produces the ground state oxygen. What a fantastic, fundamental role is played by $NO_2$. Then this becomes very vital and this becomes very basic unit; so equation 1 and 2 are very important.

So let us try the chemistry and whatever we have learnt we will try to build a model on this one. Let us try to build the model. Now apart from this, let us not forget, we may also have NO in the atmosphere, we have power plants, we have automobiles running in and out. So we have NO there and this can also react with ozone to form the $NO_2$ and back to oxygen. This I noticed again available this one; so it appears to be more like the closed things and it might be a steady state situation.

Let us write the chemistry and kinetics for this one. Let us write about $NO_2$; where is $NO_2$formed? First talk about the losses of $NO_2$; dc by dt equals to minus kc. The environment engineers understand this thing; you know fundamentally - dc by dt equals to minus kc, that is loss. Observe also if the $NO_2$ is being formed from reaction 3? Who is forming it? Ozone and NO - their product; simple. Keep this from there. Now, I can write from the nascent or atomic oxygen, which is at the ground state. Can you see how it is being formed?

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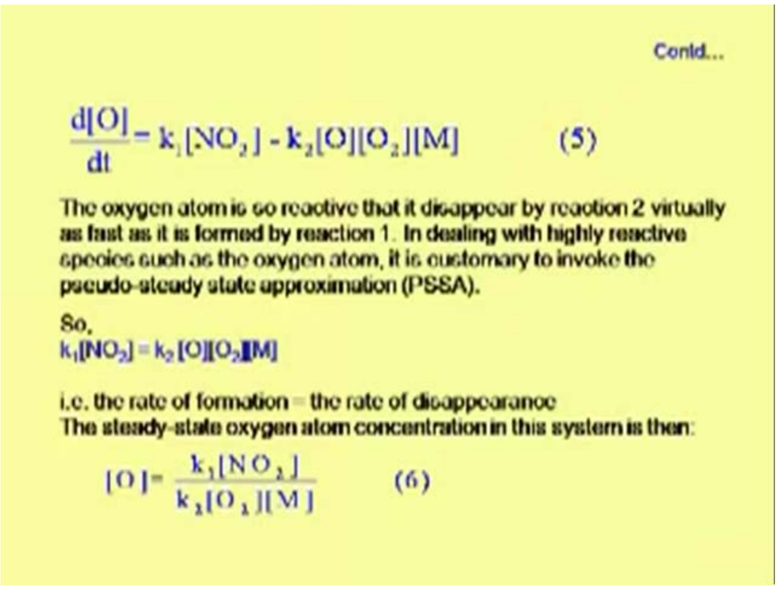

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$$\frac{d[O]}{dt} = k_1[NO_2] - k_2[O][O_2][M] \qquad (5)$$

The oxygen atom is so reactive that it disappear by reaction 2 virtually as fast as it is formed by reaction 1. In dealing with highly reactive species such as the oxygen atom, it is customary to invoke the pseudo-steady state approximation (PSSA).

So,

$k_1[NO_2] = k_2[O][O_2][M]$

i.e. the rate of formation = the rate of disappearance

The steady-state oxygen atom concentration in this system is then:

$$[O] = \frac{k_1[NO_2]}{k_2[O_2][M]} \qquad (6)$$

It has been formed by breaking of $NO_2$ plus reaction constant is $k_1$. $NO_2$ where is it disappearing? It is forming ozone reaction 2 k two. Simple. Let us proceed further. The oxygen will be so reactive that it disappears by reaction 2 virtually as fast as it is formed by reaction 1. So what situation we are getting into? Quasi or pseudo steady state. Getting in that situation; so in dealing with the highly reactive species such as the oxygen atom, it is customary, it is reasonable, to invoke the pseudo-steady state constant. So then if it is steady state, it means the change in concentration with time is 0. You can find out what will be the concentration of O, which will depend on $k_1$, $k_2$, $NO_2$ and oxygen. Is that not the thing we have done? You just need to measure $NO_2$ and NO and we might be able to say something about ozone and how much ozone will form? If I also want to.... Have you made some mistake here? I am sorry we are still dealing with the O. That will come in the next tab; we have not talked about ozone by the way; my mistake.

Equation 4 at the steady state. What was equation 4? I did not look at the screen and I went ahead. Equation 4 - at this steady state this becomes 0. $O_3$ will be something. It is very simply $k_1$ times $NO_2$ by $k_3$ NO. (Refer Slide Time: 40:37 min)

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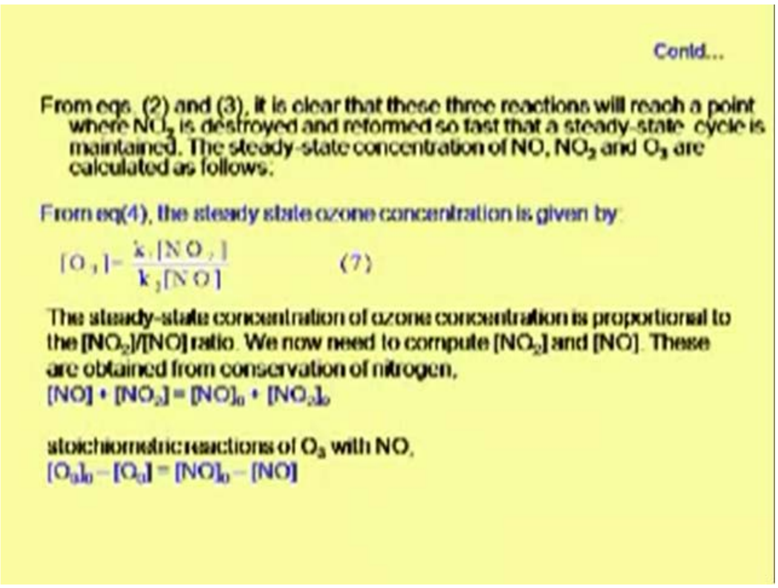

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From eqs. (2) and (3), it is clear that these three reactions will reach a point where $NO_2$ is destroyed and reformed so fast that a steady-state cycle is maintained. The steady-state concentration of NO, $NO_2$ and $O_3$ are calculated as follows:

From eq(4), the steady state ozone concentration is given by

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]} \qquad (7)$$

The steady-state concentration of ozone concentration is proportional to the $[NO_2]/[NO]$ ratio. We now need to compute $[NO_2]$ and $[NO]$. These are obtained from conservation of nitrogen,

$[NO] + [NO_2] = [NO]_0 + [NO_2]_0$

stoichiometric reactions of $O_3$ with NO,

$[O_3]_0 - [O_3] = [NO]_0 - [NO]$

This is steady state concentration ozone. Concentration is proportional to the ratio of $NO_2$ to NO because $k_1$, $k_3$ will be another constant. We now need to compute $NO_2$ and NO and we have to guide $NO_2$ and NO. Now we will do little work to modify this model; this concentration at what time? This concentration is at this steady state, at the current condition, when we are in steady state. Let us model it - how things can happen with time and if we start with some initial concentration; see these things are triggered you have to have something happening, then you get to the situation.

Since we have developed the models, we will use the model to say: what are the concentrations with time? What are the other steady state concentration? What will happen to NO and what will happen to $NO_2$? What we are saying here is... to start with, at time t is equal to 0, NO was 0, $NO_2$ was some concentration 0, ozone was some concentration 0. So we are more or less taking a big chamber and in the chamber we started the reaction and start observing them.

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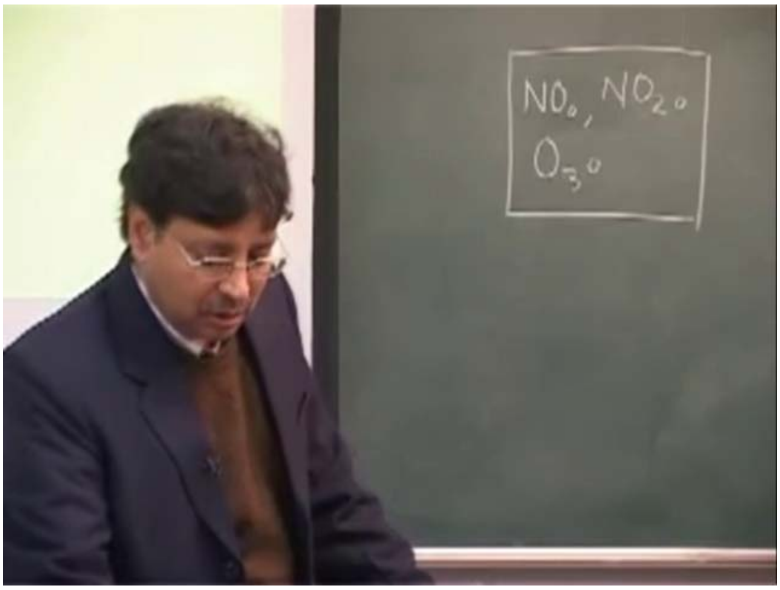

We have NO 0, $NO_2$ 0 and $O_3$ 0; initial concentrations or initial levels. Then you need to solve this one. What we had already written, but then quickly some conditions that we need to take, let us go down there, I need certain information. Nitrogen has to be balanced.

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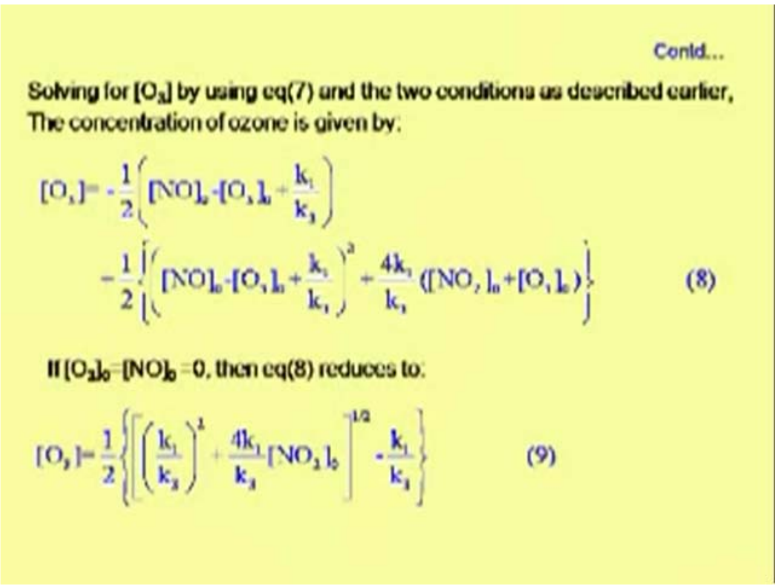

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Solving for $[O_3]$ by using eq(7) and the two conditions as described earlier, The concentration of ozone is given by:

$$[O_3] = -\frac{1}{2}\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right) - \frac{1}{2}\left\{\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}\left([NO_2]_0 + [O_3]_0\right)\right\} \qquad (8)$$

If $[O_3]_0 = [NO]_0 = 0$, then eq(8) reduces to:

$$[O_3] = \frac{1}{2}\left\{\left[\left(\frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}[NO_2]_0\right]^{1/2} - \frac{k_1}{k_3}\right\} \qquad (9)$$

NO plus $NO_2$ because they are not there, the NO, nitrogen is either in the form of NO or in the form of $NO_2$. It is not nitrate; it is not $N_2O_5$ or something; so it means mass conservation should be true. You can also see that change in the ozone will totally depend completely on change in the nitrogen species. With this knowledge we can solve the equation. As a result you can find out the ozone. It all depends you know, if it is at steady state, no doubt about it, but this is what is the initial concentration you started with. It is steady state; do not forget that we have invoked steady state conditions, but we started with this picture. What is the picture? That at the steady state that you can solve this one with the information we have got. Try to do this one because this is important. It takes a little while, it is not really straight forward, but then it is basically algebra, nothing more than algebra.

So you see here, with all this knowledge we had, I can now depending on for example, the Kanpur basin, I can see early in the morning what is the emission of NO, what was the $NO_2$, what was the ozone, if it was there, and I can try to predict the ozone concentration at steady state. So this, this, this, this, this, this (Refer Slide Time: 51:00 min). Suppose there was no initial ozone or no NO was there, then this will reduce to this; you can see that again, simple algebra again. What if I had no $NO_2$ and I had no NO? What should happen?

If there is no NO, $NO_2$ cannot be formed. If there is no $NO_2$ can ozone be formed? No that means no ozone is formed. The only way the ozone will be formed remember is the photodisassociation of $NO_2$ in the range of (($h_{mu}$)) which was less than 435 or something. So if you put $NO_2$, it goes to 0 in this module; this is already 0, so you put this $NO_2$; what is ozone concentration? Ozone concentration is 0. So this is what is the fundamental thing. So this modelling was done; so let us have a look of the results of the model.

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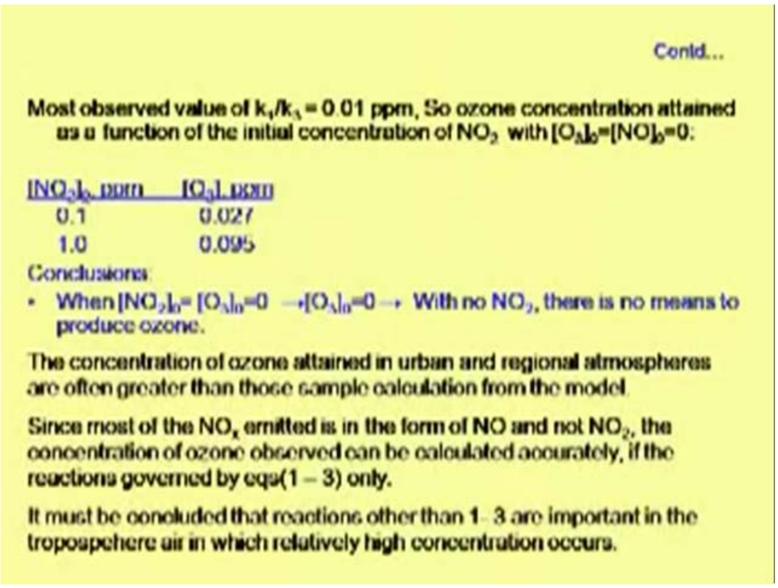

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Most observed value of $k_1/k_3 = 0.01$ ppm, So ozone concentration attained as a function of the initial concentration of $NO_2$ with $[O_3]_0=[NO]_0=0$:

| $[NO_2]_0$, ppm | $[O_3]$, ppm |
|---|---|
| 0.1 | 0.027 |
| 1.0 | 0.095 |

Conclusions:

- When $[NO_2]_0 = [O_3]_0 = 0 \rightarrow [O_3]_0 = 0 \rightarrow$ With no $NO_2$, there is no means to produce ozone.

The concentration of ozone attained in urban and regional atmospheres are often greater than those sample calculation from the model.

Since most of the $NO_x$ emitted is in the form of NO and not $NO_2$, the concentration of ozone observed can be calculated accurately, if the reactions governed by eqs(1 – 3) only.

It must be concluded that reactions other than 1- 3 are important in the tropospehere air in which relatively high concentration occurs.

People run the model and they took 0.1 as $NO_2$ at the initial stage; no NO was taken because we know that from $NO_2$ it will be formed. Then what is the ozone concentration that was predicted from the model? .027, as with one, it was produced at 0.095.

No theory, no science is complete without having tested it on the feet. All this we did from more or less from theory. When the people went out and measured, when they had such kind of concentration in the atmosphere, not a controlled situation like this, they had such a situation in the atmosphere. They knew what the ozone levels what they got were very high, higher than the numbers you are getting here. So, in a way, I am sorry to say, the model failed. With all our science the failure is, as I would say, a step towards the right direction; towards the future research. If you fail with your theory, do not be disappointed. It certainly tells you that you have not understood the process.

You can read this. The concentration of ozone attained in urban and regional atmospheres are often greater than those sample calculations from the model, as you see here. Since most of the $NO_X$ emitted is in the form of NO and not $NO_2$, the concentration of ozone observed can be calculated accurately, if the reaction is governed by the equation 1- 3 only. It must be concluded that reactions other than 1-3, something more is happening which we have not thought of. This whole thing was given by two scientists called Haggen and Smith. They kept on publishing, after 1952, lots of great papers on this field.

So what we will do is, we will stop here and try to answer the question: as to why our model failed? Snd how we can rectify the mode? This  we should be able to. If these people coming in 1952 can give some answers we should able to at least say what is ozone that will be formed here.