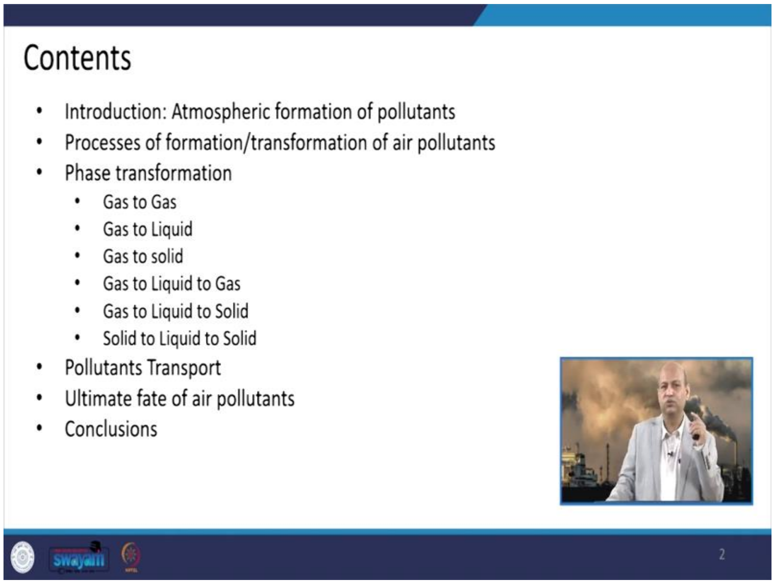
Air Pollution and Control
Professor Bhola Ram Gurjar
Department of Civil Engineering
Indian Institute of Technology, Roorkee
Lecture 08
Atmospheric Formation and Fate of Air Pollutants

Hello, friends. You may recall last time we discussed about sources and classification of air pollutants. So, today we will discuss atmospheric formation and fate of air pollutants. That means, we will see for example, when pollutants are emitted and they enter into the atmosphere, then what happens to them. They basically get converted into secondary air pollutants or they get deposited or they get transported from one place to another.

So, from source to the receptor a lot of things happen. Their physical chemical characteristics may change and they may also get transformed into another kind of phase. For example, gas pollutant, gaseous pollutants can get transformed into like liquid form like droplets they get into moisture, and all those. They can get converted into solid particles, that is particulate matter. So, the phase transformation may also happen.

So, you can say there are atmospheric formation of new air pollutants. So, we will see what are the processes of those formation and transformation of air pollutants, when they get into the atmosphere.

(Refer Slide Time: 01:42)



So, in that framework we will see the phase transformation, like gas to gas, means, another gas like CO can get converted into CO_2. Then gas to liquid. So, for example, SO_2 can get converted into H_2SO_3, H_2SO_4, like that. Then gas to solid means, like calcium sulphate is formed in the presence of calcium particles and SO_2, moisture all those things. So, then it may also happen that gas to liquid to gas, gas to liquid to solid, solid to liquid to solid particles can get also converted into another form.

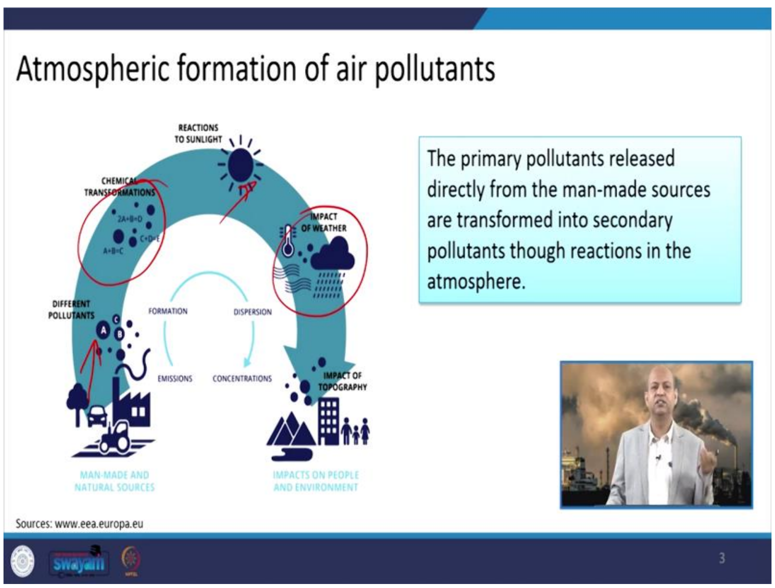
Then pollutants also transport. So, transformation and transportation, both things happen. From the source to the receptor, as I said, when it is emitted, pollutants are emitted, so, they will be transformed into something. When they reach to the destination, in between they will be transformed into some other pollutants also. Although original pollutants may also be there and depending upon the concentration.

Their lifespan may increase if highly concentrated pollutants are there, but at the same time because of atmospheric processes, that transformation will, will happen, and transportation will happen so that they can reach to the destination. Whatever destination, it can be thousands of kilometer, downwind direction or within one kilometer they can drop down with the process of gravity if particles are large in size those kinds of things. So, that transportation will also we will study.

Then ultimate fate of the air pollutants. So, what happens ultimately, where do they go, or how they are removed from the atmosphere, what is that process and what are other atmospheric constituents that play a significant role in cleaning that atmosphere. So, you might have heard about like self cleansing capacity of rivers or water bodies.

Similarly, atmosphere also has self cleaning capacity or self cleansing capacity because hydroxyl ions are there, those radicals are there. So, they take part and oxidation happens very rapidly, then, there may be some ozone or other pollutants, which may also do some scavenging kind of things. So, that decides the ultimate fate of the air pollutants. Ultimately, we will conclude.

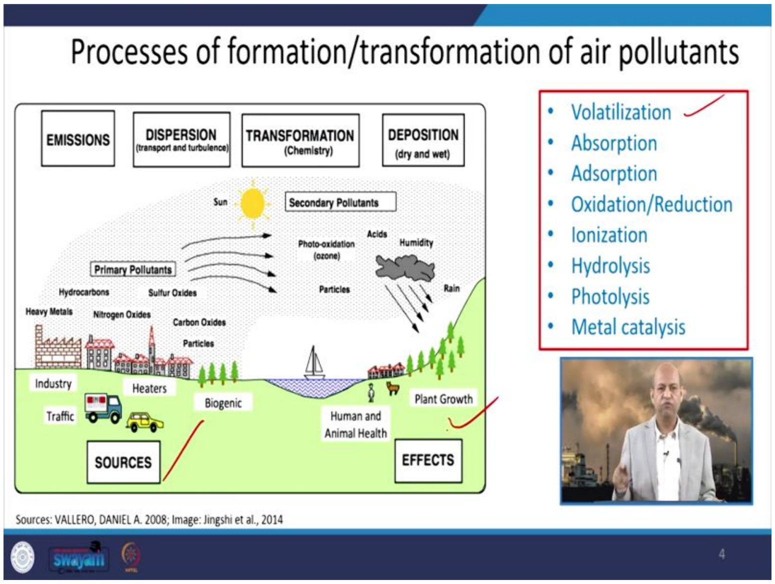
(Refer Slide Time: 04:21)



So, let's start. Like atmospheric formation of air pollutants. So, here it is shown that different pollutants are being emitted from various anthropogenic activities. Then chemical transformation is happening in the atmosphere. And in the presence of the sunlight, some photochemical reactions may also happen, like ozone production may happen. Then they also interact with the like cloud formation. Small particles contribute into nucleation. So, condensation happens and cloud formation happens.

So that way, pollutants, those particles, they get down with the precipitation and it is called as wet deposition or precipitation. Sometimes solid deposition also happens, means particles they comes down, they come down to the surface. So that is known as the dry deposition. So those things happen and ultimately they get into, attached to the surfaces of the buildings or we inhale, animals inhale, they become part of the ecosystem and water bodies, everywhere they can get into the particular system.

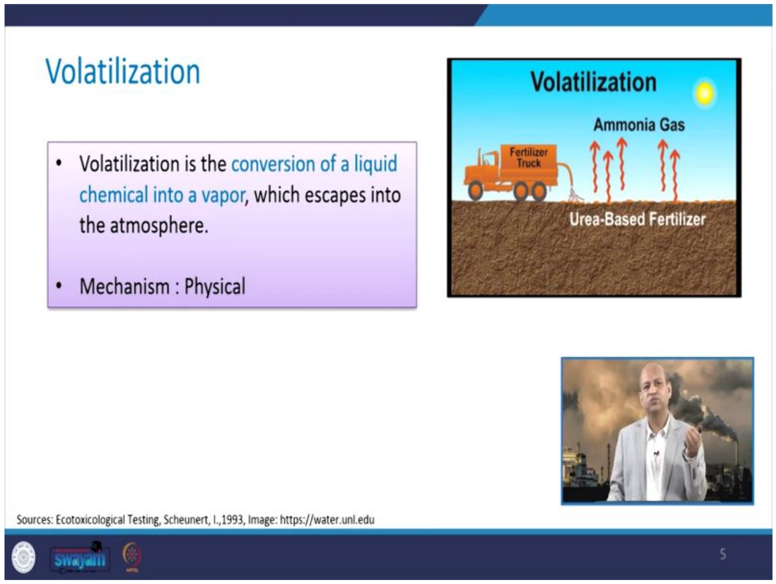
(Refer Slide Time: 05:29)



Well, so, the processes of formation and transformation of air pollutants can be listed like volatilization, absorption, absorption, oxidation/reduction process, ionization or hydrolysis or photolysis or metal catalysis, all these things happen in the atmosphere. So, we will see those processes.

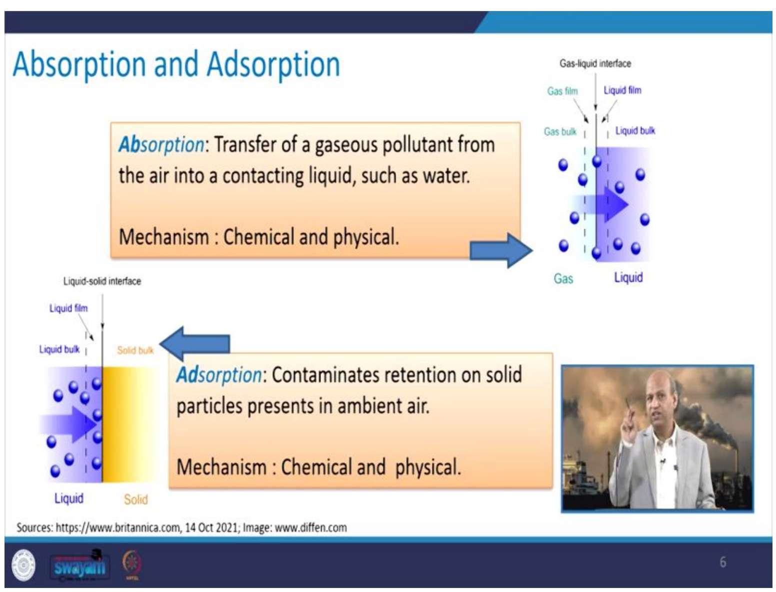
And you can see in this pictorial representation, very nice representation, from the source to the receptor, you can see like those, whether heavy metals from factories or hydrocarbons, these are the primary pollutants. They get converted into some secondary pollutants because of chemical reactions and this photo-oxidation happens, this ozone, then acidic formation maybe, humidity will play the role, rain happens then they become part of this rainwater and all those water bodies get affected. So, the source and the receptor where this effect is visible.

(Refer Slide Time: 06:35)



So now, we see the volatilization. In this process basically the conversion of a liquid chemical into vapor because of this temperature and pressure, those physical processes there. So volatile compounds are there. You might have heard VOCs, Volatile Organic Compounds. Like, on the petrol pump, you have some smell, because those gasoline they have hydrocarbons they can form vapor. So that vapor is there and this is because of these VOCs, Volatile Organic Compounds, they become part of air pollution.

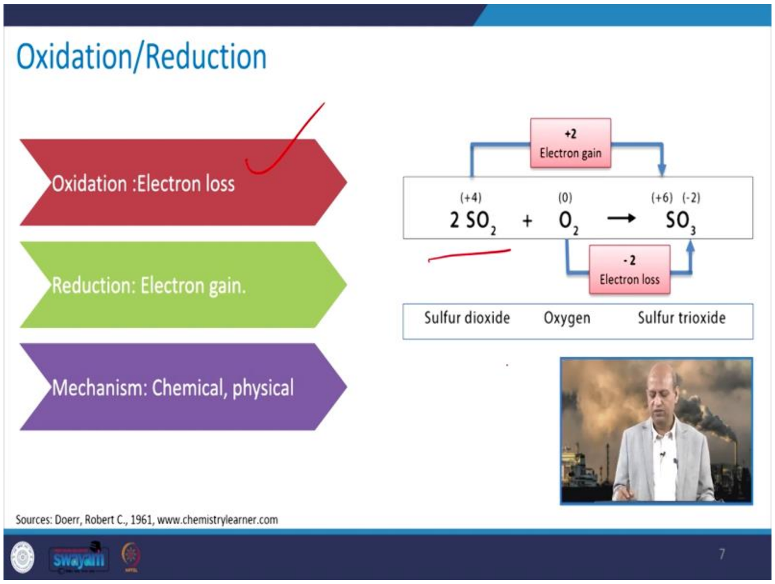
(Refer Slide Time: 07:15)



Well, then absorption and adsorption. So absorption basically, you can see like gas liquid interface it is, and the transfer of gaseous pollutants from the air into the, this liquid phase such as water. So that is chemical and physical process of course, and that becomes like as I said like SO_2 get converted into H_2SO_3 and those kinds of things. So, this is absorption in the, this droplet, liquid droplets is there.

Adsorption, on the surface, like solid surfaces maybe there, so at the surface you can have these contaminants retention on the solid particles present in the ambient air. So that is known as the adsorption. So basic difference absorption, adsorption, both are distinct processes.

(Refer Slide Time: 08:02)

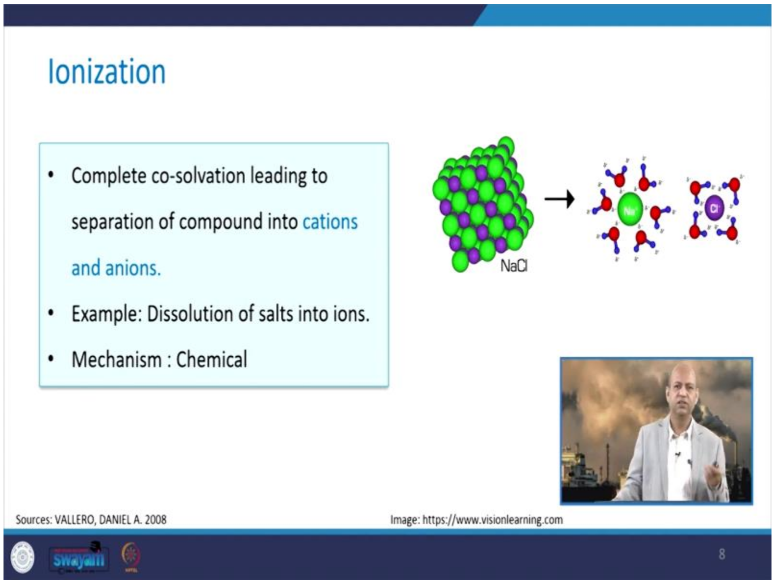


Then oxidation and reduction. You can see like sulphur dioxide is there. In oxidation, you see the loss of the electron is there, in reduction electron gain is there, and this whole mechanism is chemical and physical. So the SO_2, this is giving these electrons and then this electron loss is there of minus 2 and SO_3 formation is there.

$$2SO_2 + O_2 \rightarrow SO_3$$

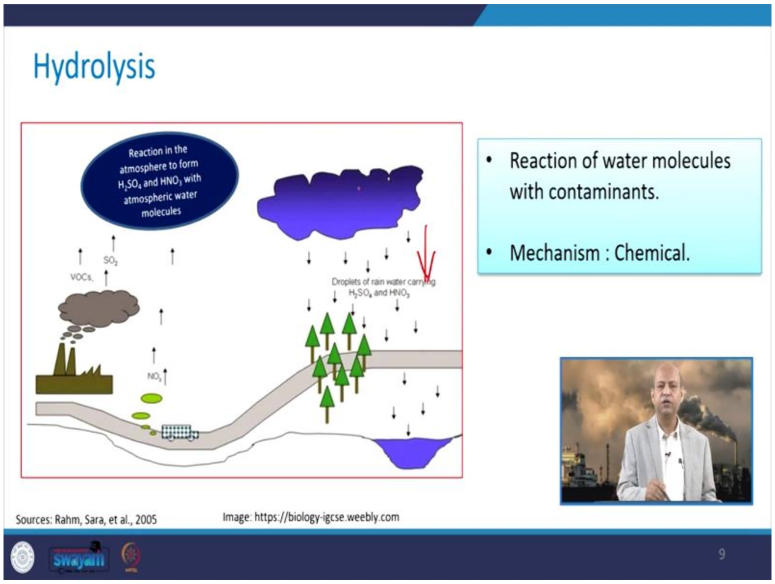
So that way you can see this oxidation and reduction process in this particular reaction or equation.

(Refer Slide Time: 08:31)



Ionization. In this basically, the complete co-solvation leading to separation of compounds into cations and anions. So that is known as the ionization. And, for an example like dissolution of salts into ions, Na^+, Cl^-, those kinds of things. This happens in atmosphere also, like at the coastal regions where saltwater is, salty water is there and with the strike of the air, this partition happens and some chemical processes may also happen in the air and that can break these and they can get converted into Na^+, Cl^-.

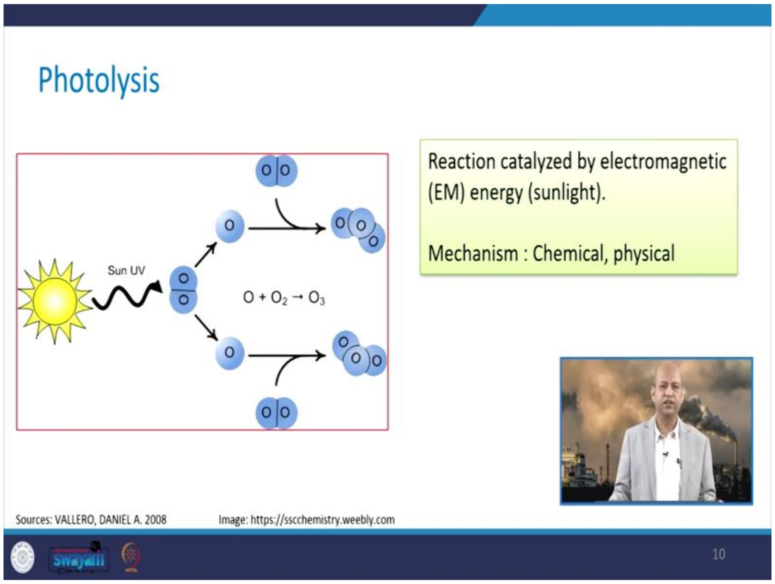
(Refer Slide Time: 09:16)



So, after ionization, we discuss about hydrolysis. In hydrolysis, like this SO_2 goes into the atmosphere in the presence of H_2O, this becomes part of like, reaction of producing H_2SO_3, then H_2SO_4. Similarly, NO_X or NO_2, they get converted into HNO_3 because of this moisture.

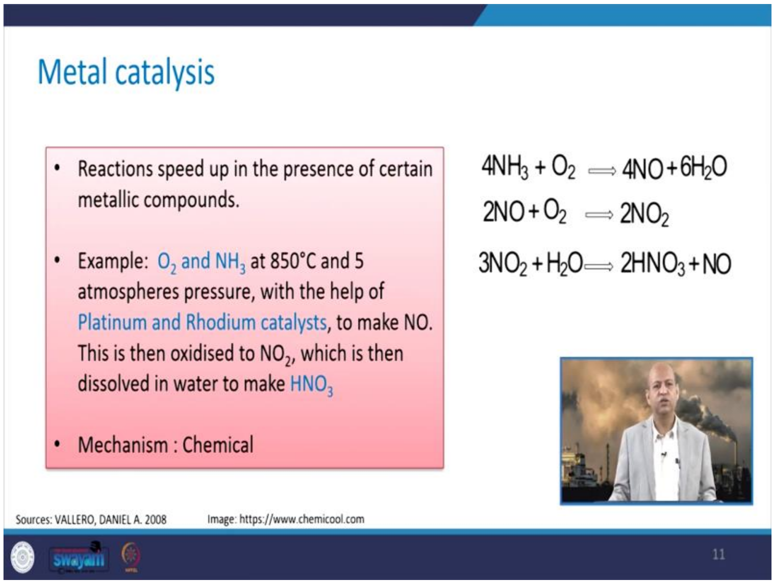
So, this hydrolysis process is there and they become part of this, cloud precipitation from the clouds droplet, in the form of droplets. So, the acid rain basically formation is the result of this hydrolysis. And this is reaction of water molecules with the contaminants present in the atmosphere. And this mechanism is known as chemical process, you can say.

(Refer Slide Time: 09:52)



Similarly, like photolysis is there in the presence of sunlight. So the ozone production happens because of photolysis as you know. And this reaction catalyzed by electromagnetic energy which is from the sunlight. And this physicochemical process can be taken into account with the presence of sunlight. So we will see how this ozone is produced.

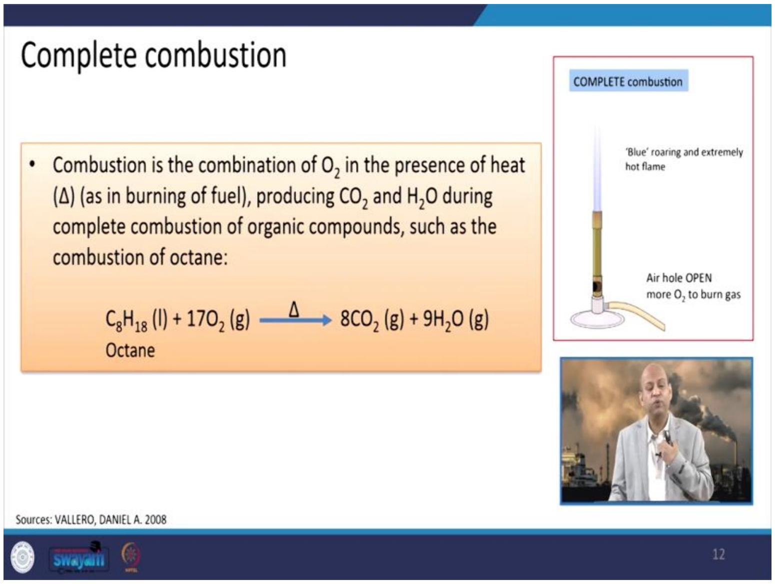
(Refer Slide Time: 10:16)



Well, this metal catalyst is formation this reaction is also there, which speeds up in the presence of certain metallic compounds. And the examples are like oxygen and ammonia. At 850 °C and 5 atmospheres pressure (atm), with the help of platinum and this rhodium catalysts to make this nitric oxide.

And this is then oxidized to nitrogen dioxide which is then dissolved in water to make HNO_3. So this is a chemical process, and this is known as the metal catalysis, the reaction, the whole reaction is shown here.

(Refer Slide Time: 10:58)

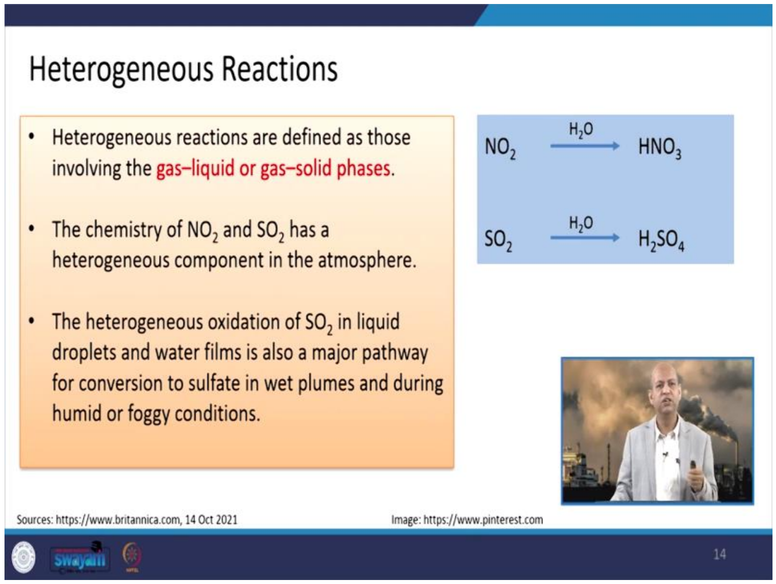


Well, as you know, whatever pollution is becoming from the fossil fuel burning etc, that is the result of combustion. When complete combustion happens then for example, like hydrocarbons are there, fuels are basically hydrocarbon as you know, so they get completely oxidized. So that means they get completely converted into CO_2 and H_2O. And as such, CO_2 and H_2O are harmless from air pollutants point of view.

So that is why we talk that we should go for carbon neutral fuels so that extra CO_2 is not dumped into the, or emitted into the atmosphere because that caused this global warming, climate change related issues. So the complete combustion from air pollutants point of view, it is fine because in complete combustion, they give some unburnt hydrocarbons, VOCs, CO, all these are air pollutants, they are very harmful for our health etc.

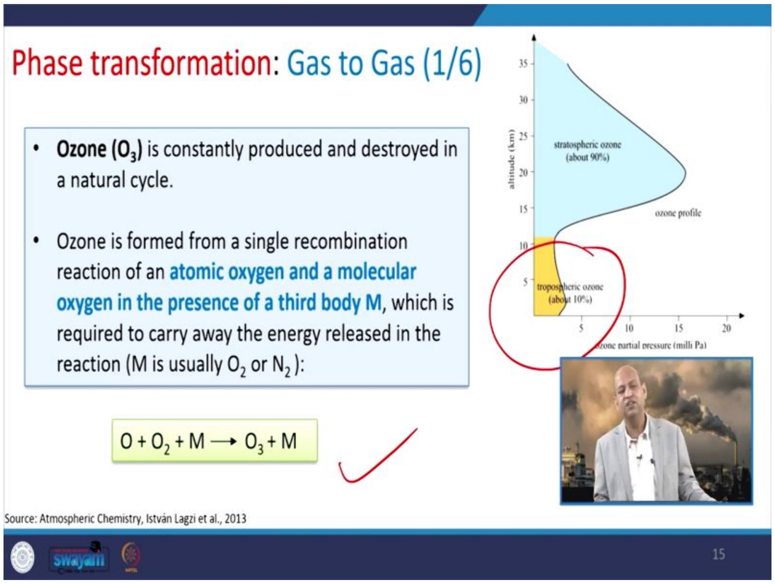
So complete combustion in that sense is good, but from global warming from greenhouse gas point of view, we do not want extra CO_2 and H_2O etc, but we cannot get away with this at present at least. And incomplete combustion like this production of dioxins CO or this polycyclic aromatic hydrocarbons part is known as PAHs. So all these are the products and of incomplete combustion, and they are very toxic pollutants.

(Refer Slide Time: 12:50)



Then there is, there is this heterogeneous reactions are also there, like gas to liquid, gas solid phase, those kind of reactions maybe there. Like NO_2, SO_2, they get converted into HNO_3 and H_2SO_4. So these are heterogeneous reactions which also happen in the atmosphere. So three reactions may happen, complete combustion, so those greenhouse gases CO_2, H_2O etc, or incomplete combustion, then of course, certain pollutants and these heterogeneous reactions can get phase transformation from gas to liquid or so.

(Refer Slide Time: 13:19)

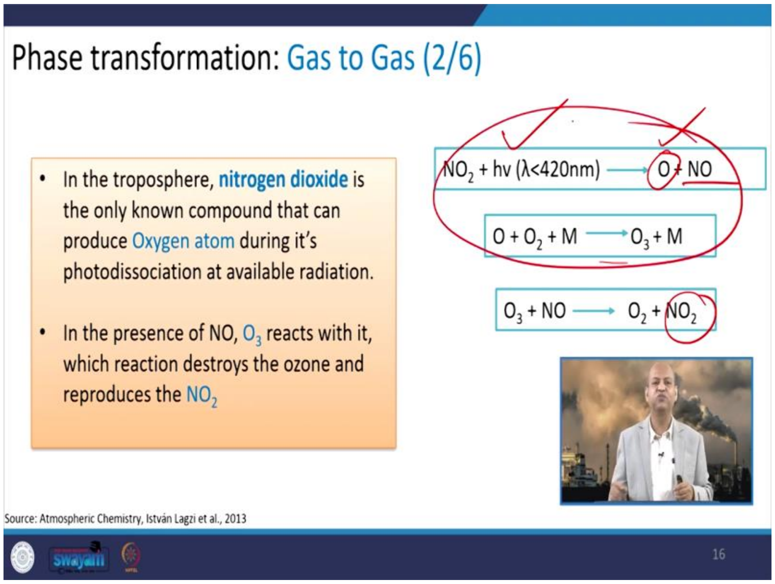


Now, in detail we go through this phase transformation, like gas to gas. So the gas to gas for example, in the presence of carbon monoxide or nitrogen dioxide or volatile organic compounds, ozone production is there if sunlight is there. And this particular ozone formation is kind of single recombination of reaction of atomic oxygen and a molecular oxygen in the presence of a third body which is kind of like O_2 or N_2, those kinds of things are present.

Then they participate in the reaction and produce the ozone, you can see here. And in the stratosphere this particular reaction happens, and 90 percent of ozone is produced in a stratosphere, but that is good for us, as you know, because that protects us from ultraviolet rays.

But in this troposphere, this 10 percent of the total atmospheric ozone is there, this is harmful, very harmful for us. We do not want it, but still it is produced in the presence of sunlight if precursors are there. And what are those precursors? Like NO_X, NO_2 and then these VOCs, CO, methane all these are these precursors.

(Refer Slide Time: 14:39)

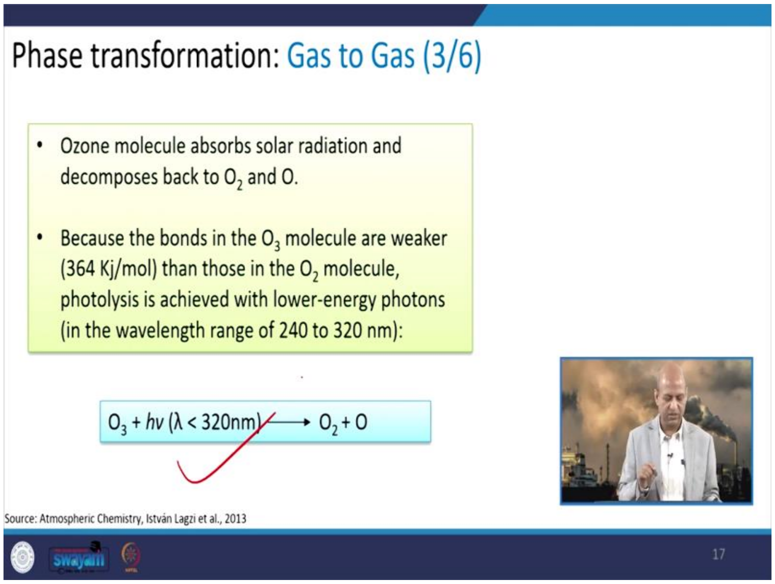


So here you can see this phase transformation again. The explanation through nitrogen dioxide, which is the only known compound, basically, that can produce oxygen atom during its photodissociation in the presence of this radiation. You can see here this O (oxygen atom) is there, NO is there. NO_2 from NO_2, it can be there.

Then this O is available for reaction with this O_2. So ozone is produced. And O_2, this ozone can react with NO and produce NO_2 also. This is very interesting reaction, or this is also known as titration, atmospheric titration. And this, this particular reaction is responsible that in the city centers where a lot of emission of NO is there, nitric oxide is emitted from vehicular emissions, so that destroys ozone.

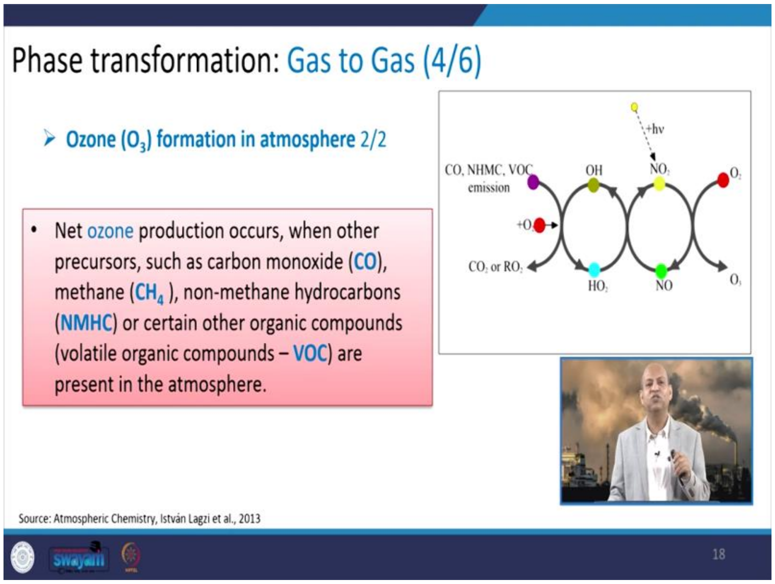
So that is why at city centers you do not find much ozone. But this NO_2 goes in the downwind direction in the countryside with a lot of sunshine is there. So in countryside or rural areas, this NO_2 will produce again ozone by this kind of reaction. So that is very interesting thing, you should remember.

(Refer Slide Time: 15:54)



Now, this, this ozone molecule absorbs solar radiation and it can also get decomposed back to Oxygen. So this kind of reaction can happen.

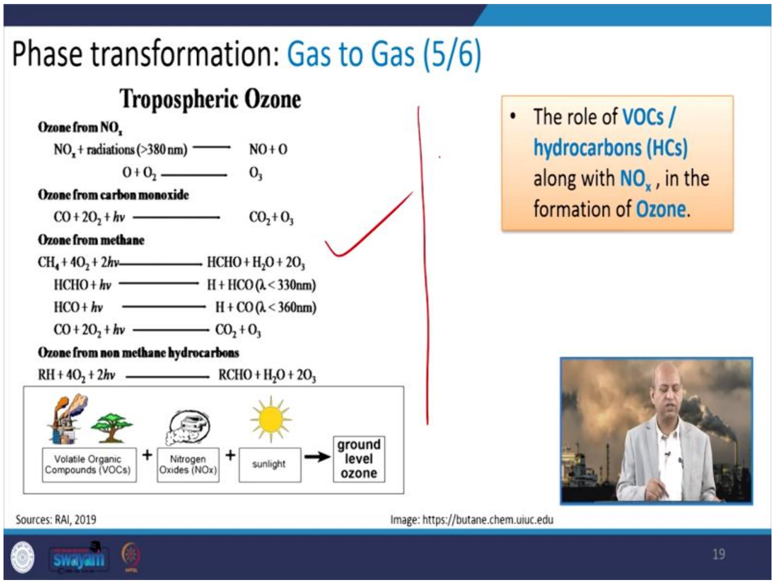
(Refer Slide Time: 16:06)



And then, basically net ozone production occurs when other precursors such as carbon monoxide or methane, non-methane hydrocarbons (NMHC) or certain other organic compounds like volatile organic compounds, VOCs are present in the atmosphere. So those different precursors are available.

Then the nitrogen production may take place in the presence, but sometimes ozone production is driven by NO_X, sometimes it is driven by VOCs and we have to know which is controlling this reaction, otherwise, the ozone production cannot be reduced if you do not know which particular reaction is dominating in that area.

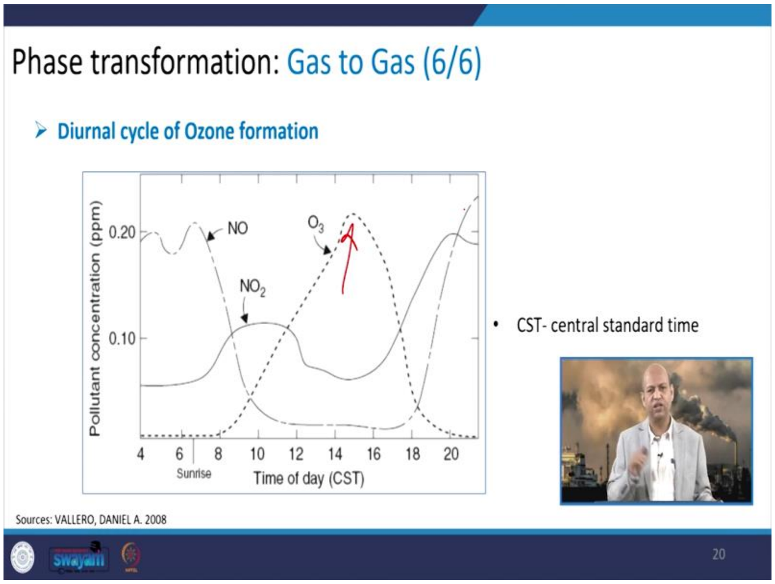
(Refer Slide Time: 16:47)



So ultimately this gas to gas transformation can be nicely depicted in this particular set of reactions, where NO_X is converted into NO and O, and ozone is produced, CO also gives the like CO_2 and this ozone, and this methane also can produce ozone, and then this, these are the radicals which, which can participate, and the ground level ozone production can be there.

So the role of VOCs or hydrocarbons along with NO_X is very important in the formation of ozone in the atmosphere. So that is very important reactions, you should remember, when we talk about ozone production.

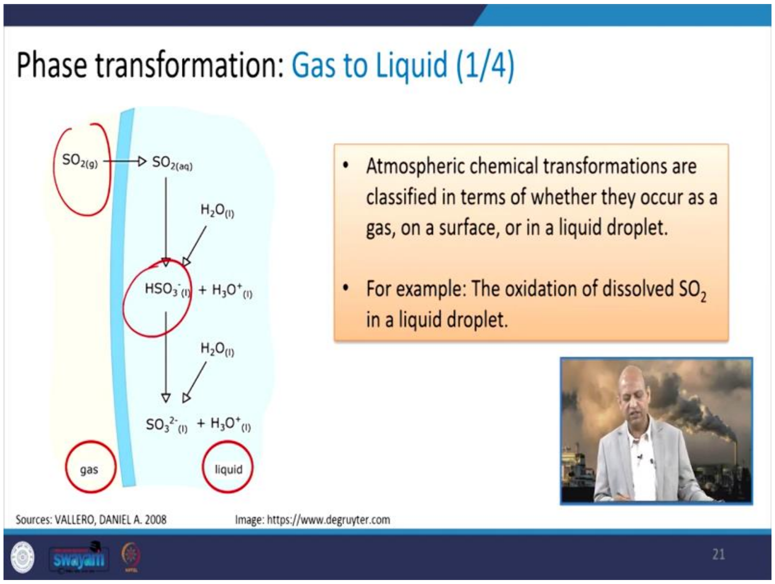
(Refer Slide Time: 17:30)



And this is responsible for this diurnal cycle. Diurnal cycle means within the day, 24 hours it changes. Like in the morning there is no sunlight. So ozone is very minimum. All ozone is, get converted, with NO it goes into NO_2 production. Then in the sunlight a lot of this ozone production is there, but NO_2 is consumed in the production of ozone. So NO_2 is less here.

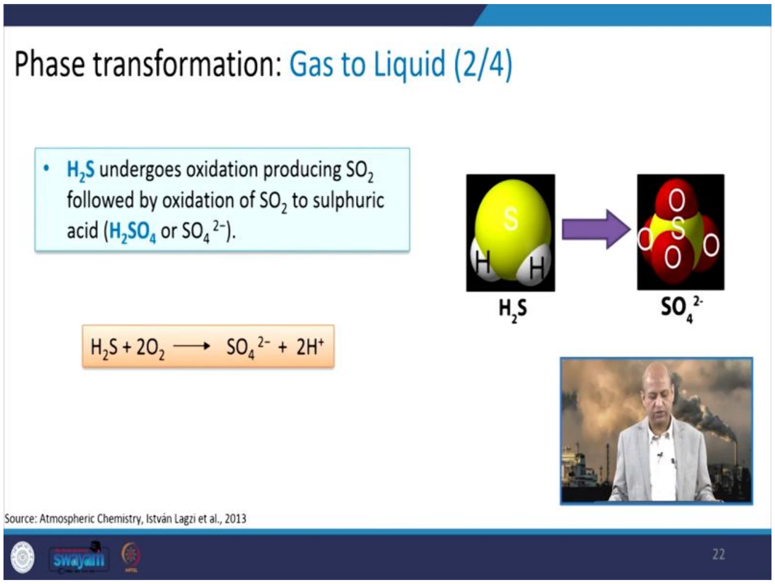
Then again ozone diminishes in the evening time and this NO starts to increase, and this NO_2 starts to increase. So that way this diurnal cycle is there. It goes up and down. And that is very again popular reaction for explaining the origin and NO_X relationship in the urban areas.

(Refer Slide Time: 18:19)



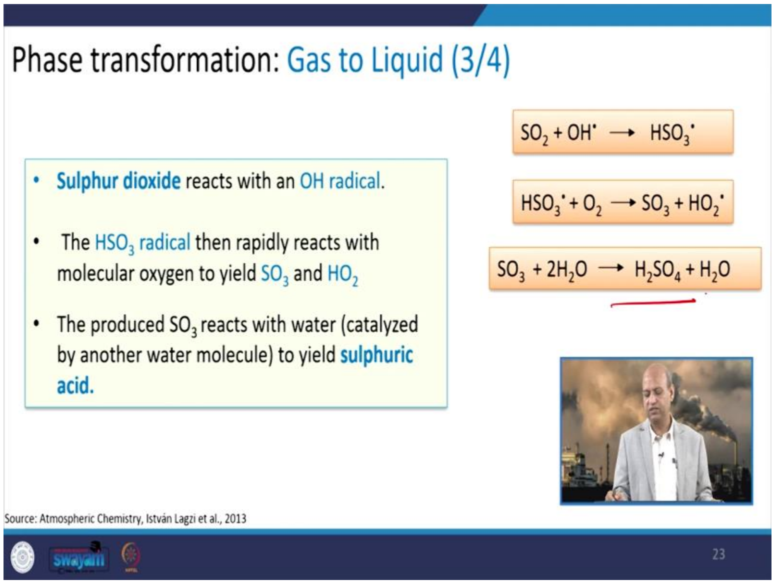
Well, the face transformation, now we go for gas to liquid. You can see here like gas, SO_2 is there, and moisture is there. So the, in the presence of moisture it can get converted into HSO_3. Ultimately, it can get converted into H_2SO_4.

(Refer Slide Time: 18:36)



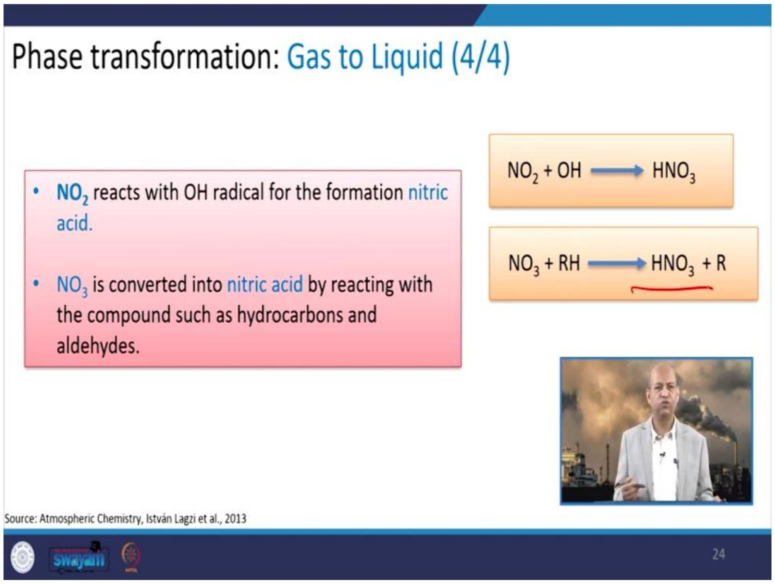
So here, you can see this H_2SO_4 production is shown in this figure as well as in, in this reaction.

(Refer Slide Time: 18:43)



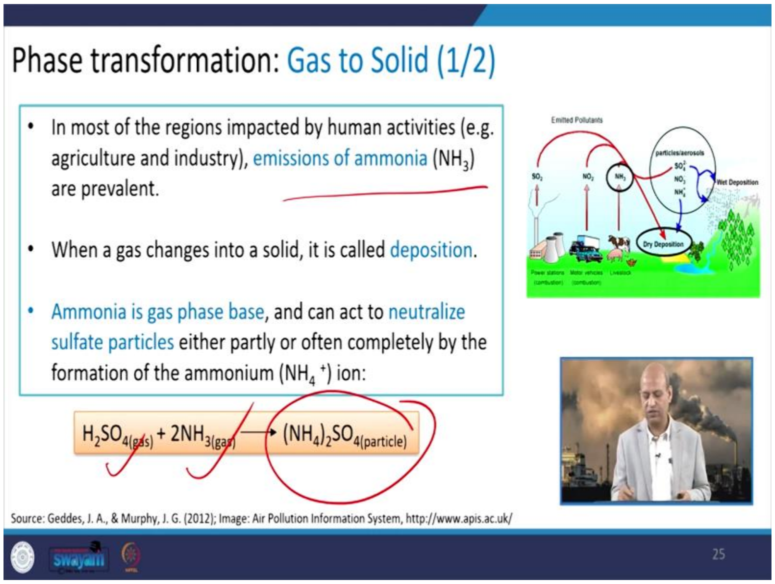
So this is the complete reaction, set of reactions where sulphur dioxide reacts with the OH radicals, hydroxyl radicals, and this HSO_3 radical then rapidly reacts with molecular oxygen to yield SO_3 and HO_2 and ultimately this sulfuric acid is produced.

(Refer Slide Time: 19:03)



Well, similarly, NO_2 to get converted into HNO_3. So this is the same gas to liquid transformation or phase transformation happens of the pollutants.

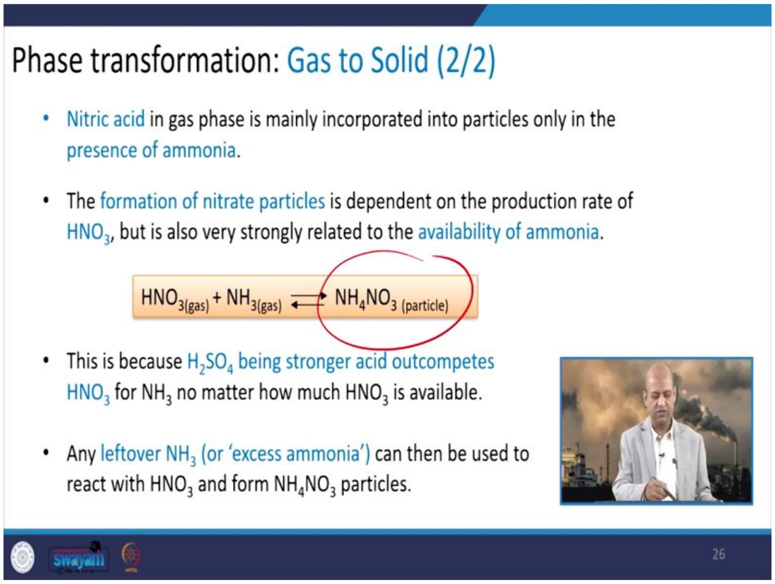
(Refer Slide Time: 19:13)



When we talk about phase transformation of gas to the solid, then basically how gaseous components get converted into particulate matter, those are secondary aerosols. Primary particulate matters are emitted directly from diesel driven vehicles and so many sources are there, coal burning, thermal power plants or anything where which you burn particulate matters are emitted, those are primary pollutants.

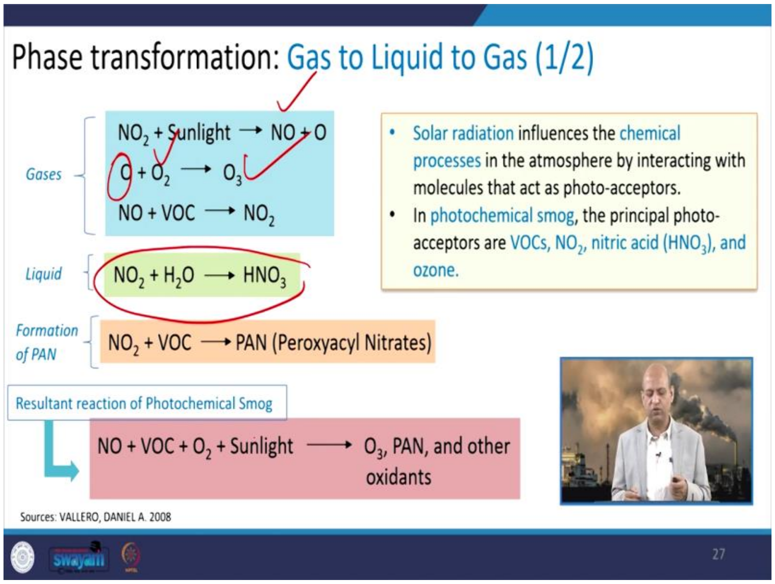
But secondary aerosols can be produced by this particular gas to solid transformation. You can here, see here emissions of ammonia, they, they get converted into like this ammonium sulphate. So the SO_2 presence, if there particles are also there, moisture is there, all those things, helping, this gas is there, this is also gas, ultimately ammonium sulphate, that is particle. So that way gas to phase, solid phase transformation can occur. You can see in this pictorial representation also, the same thing.

(Refer Slide Time: 20:14)



Then, also, this HNO_3 and ammonia, that is, ammonium nitrate, again, the particle. But this H_2SO_4, is very strong reactive acid, and that see that this ammonium sulphate is produced, that reaction is controlled by that, so the remaining ammonia if is there then ammonium nitrate may be produced otherwise that is the dominating, earlier one the dominating reaction.

(Refer Slide Time: 20:41)

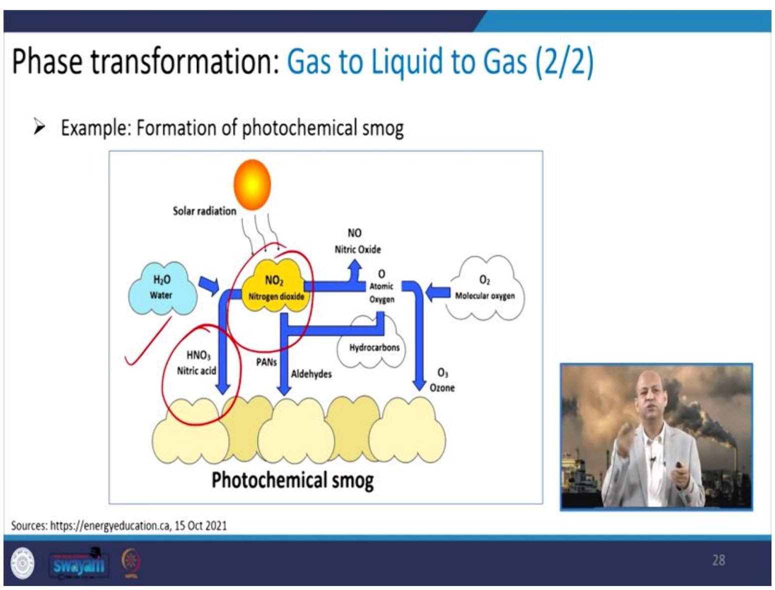


Now, if you talk about gas to liquid to gas, so three steps or two steps you can say. So here also, like gases are also shown in this particular, the same reaction of ozone production, you can see here. This NO_2 sunlight, is it dissociate into NO and O and available. So this react with the oxygen molecule and ozone is produced. And then VOC and NO, if it is there then NO_2 is produced. And NO_2 get converted into HNO_3. And NO_2 can also produce, ultimately the ozone.

So the liquid, this HNO_3, this NO_2 is taking part here with H_2O and HNO_3 is produced. So the first transformation from gas to liquid happening. Now you can see here, this is a NO_2 to plus VOC, the peroxyacetyl nitrate is produced. And this photochemical smog, nitric oxide, VOC, oxygen, sunlight was, they give ozone, PAN and other oxidants. So that way gas to liquid and then gas formation again, you can see.

So those kinds of reactions happen continuously into the atmosphere. This is a very complex reactor, the whole atmosphere is a kind of reactor. A lot of reactions are occurring there, happening there. And in the sunlight, different kinds of reactions may happen, otherwise in the presence of these liquid droplets other kinds of reactions can occur.

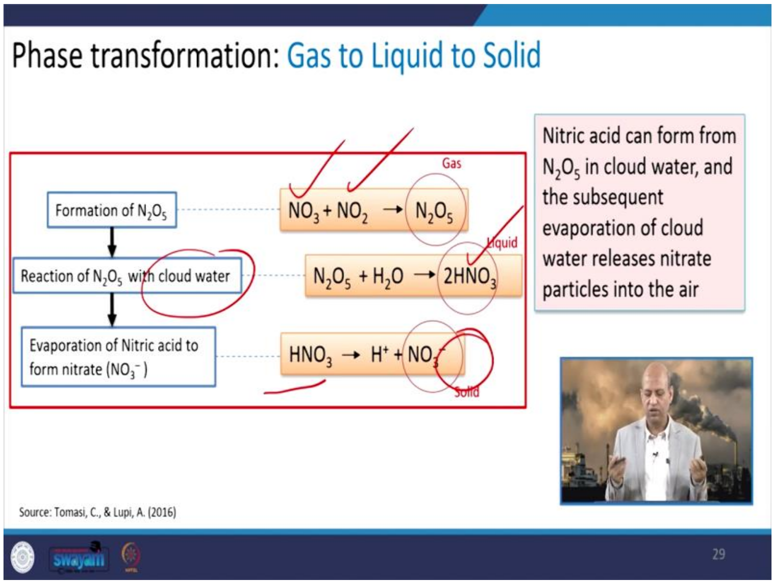
(Refer Slide Time: 22:11)



Now, again this pictorial representation is there. How this H_2O, water is there, and this photochemical smog is produced because nitrogen dioxide get converted into these kinds of liquid transformation, gas to liquid, and then gases are also there. So basically in smog, liquid droplets are also there where HNO_3 maybe present, then aldehydes maybe there, PAN is there, and hydrocarbons, all kinds of soot is there.

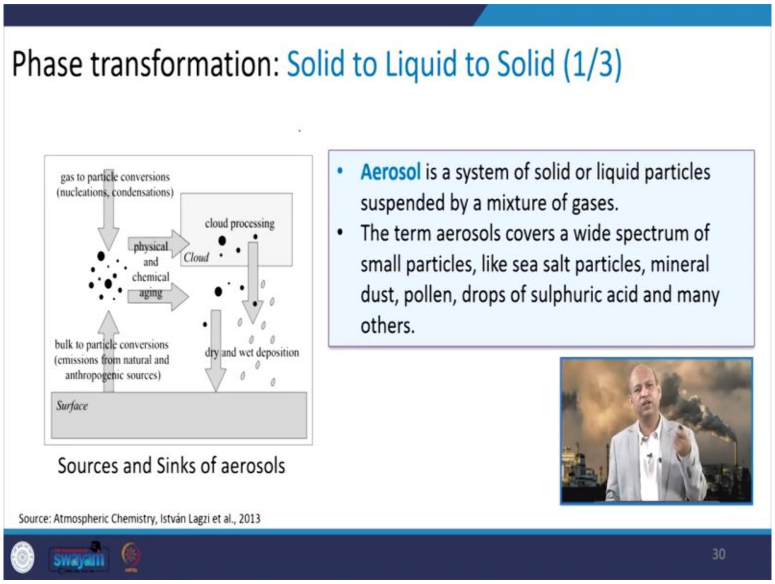
And that way the secondary aerosols may also be there, scattering of light, so visibility reduce, and brownish haze is produced in the atmosphere because of, this entity is known as the smog.

(Refer Slide Time: 22:53)



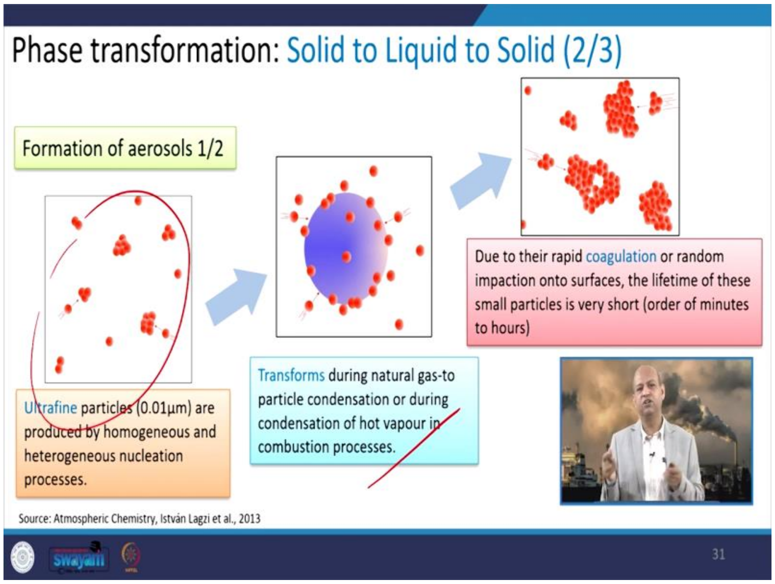
Then gas to liquid to solid, that is another interesting part, you can see here. Like, this gas is produced, formation of N_2O_5. This is NO_3, NO_2 all these gases. They get converted into gas. Then this reaction N_2O_5, with the cloud water, moisture, so N_2O_5 plus H_2O, it gives us HNO_3, liquid transformation, from gas to liquid. Now, HNO_3 get converted into again, this nitrate some sort of nitrate in the presence of other pollutants. So that is solid particle. So that we gas to liquid to solid transformation may also happen in the atmosphere.

(Refer Slide Time: 23:45)



Well now, the another phase transformation. Earlier we saw gas to liquid to solid. now, we are solid to liquid to solid. That is another way. So because of presence of these aerosols, they react with the moisture and they get transformed into liquid particles, liquid droplets, those kinds of things, and then they get deposited in terms of some particulates, some aerosols. So that is the transformation or interaction of solid to liquid to solid.

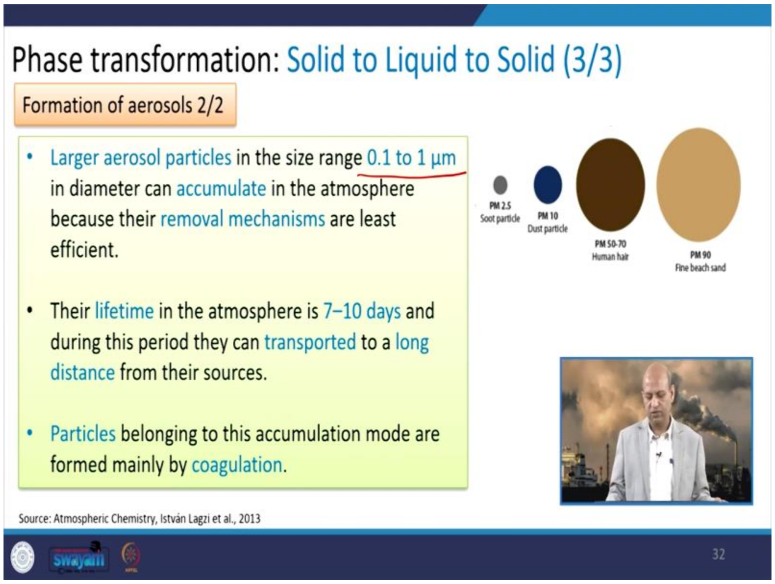
(Refer Slide Time: 24:08)



And here you can see formation of aerosols are there. So these are the solids. Ultra fine particles are produced by homogeneous and heterogeneous nucleation process. So this is the solid, formation of aerosols. Then transformation during natural gas to particle condensation or during condensation of water vapor to combustion process. So that is basically the, this liquid part.

Then due to the rapid coagulation or random impaction onto the surface, the lifetime of these small particles is very short. So this solid to liquid to solid, this transformation happens very quickly and within hours these reactions are there.

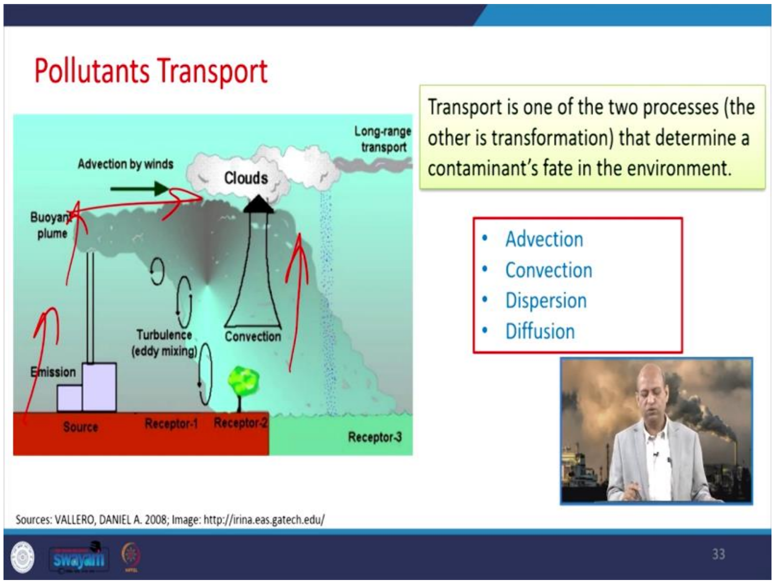
(Refer Slide Time: 24:50)



Then, this formation of aerosols are there, larger aerosol particles can be there, which are 0.1 to 1 micrometer diameter, and they accumulate in the atmosphere. And because their removal mechanism are least efficient because of their size.

Then lifetime in the atmosphere is around 7 to 10 days. They hang around in the atmosphere, and they can be transported for a long distance because of this lifetime. And particles belonging to this accumulation mode are formed mainly by coagulation. So that, depending upon the size their fate is decided basically.

(Refer Slide Time: 25:29)

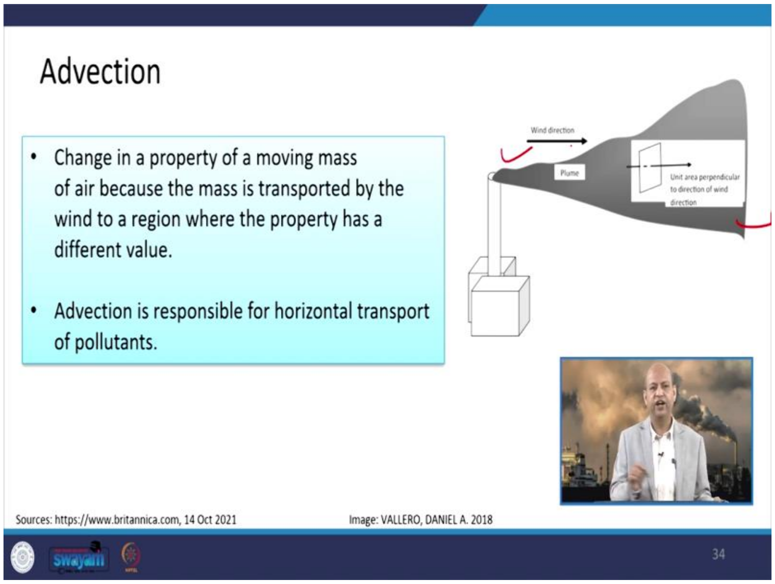


Now, we talk about pollutants transport. So here you can see emissions are happening, pollutants are coming in the atmosphere. From chimney, buoyancy, due to buoyancy or due to temperature difference that goes into atmosphere, and then because of advective currents of the winds, means horizontal movement, it goes in the horizontal direction.

Because of convection, this temperature difference and pressure difference, the vertical movement is also there, which is known as the convection. And turbulence also helps in the dispersion and diffusion of the pollutants, and ultimately they become part of clouds and they come down with the precipitation.

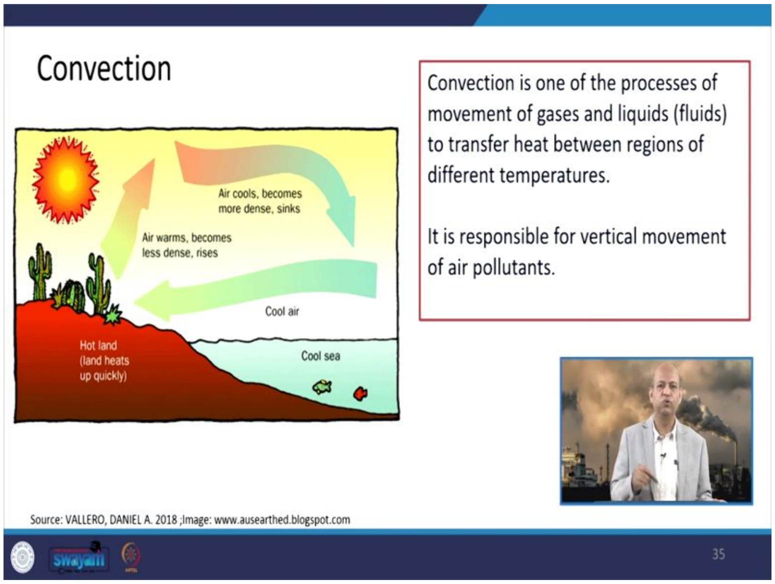
So the transportation of the pollutants basically, are governed by advection, convection dispersion and diffusion. So these processes, let us see.

(Refer Slide Time: 26:20)



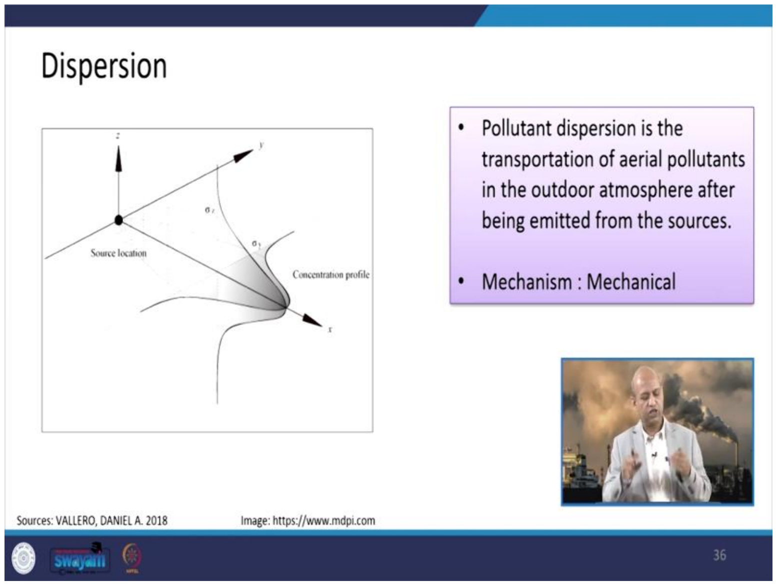
Like advection, this is nothing but change in a property of moving mass of air because of the mass is transported by the wind to a region where the, this property has a different value. So the horizontal movement or transport of the pollutants can happen from this point to this point. This is the advection process.

(Refer Slide Time: 26:42)



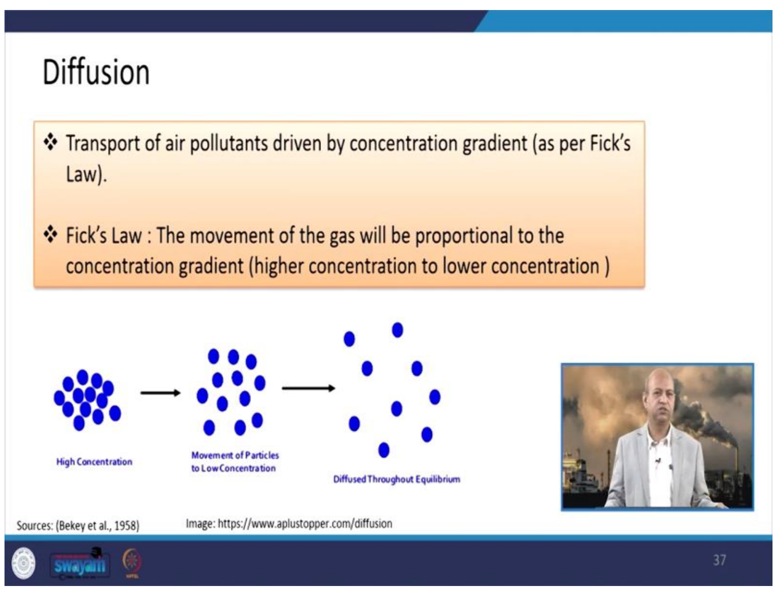
Convection, as you know, vertical movement. Convection is basically the process of movement of gases and liquids like fluids etc, due to heat transfer and in the vertical movement, because of this process. And this vertical movement is suppressed in the inversion if you know.

(Refer Slide Time: 26:56)



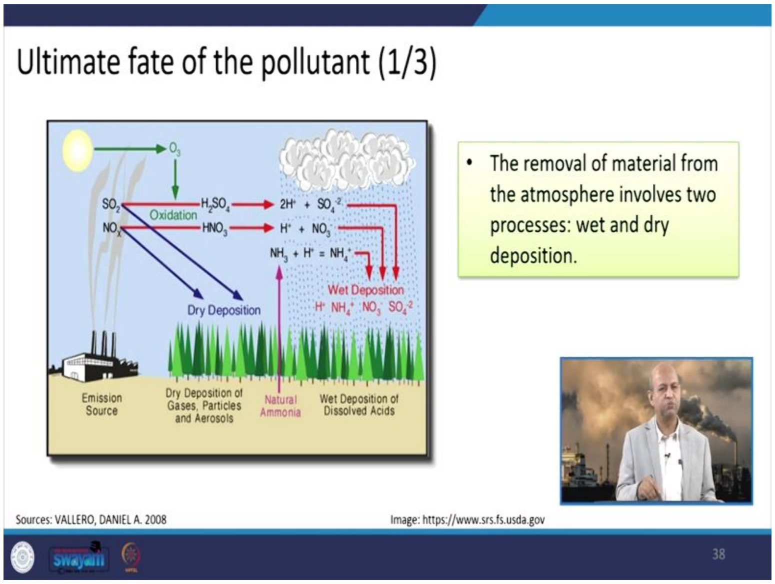
Dispersion happens, because of this turbulence and then wind movement.

(Refer Slide Time: 27:08)



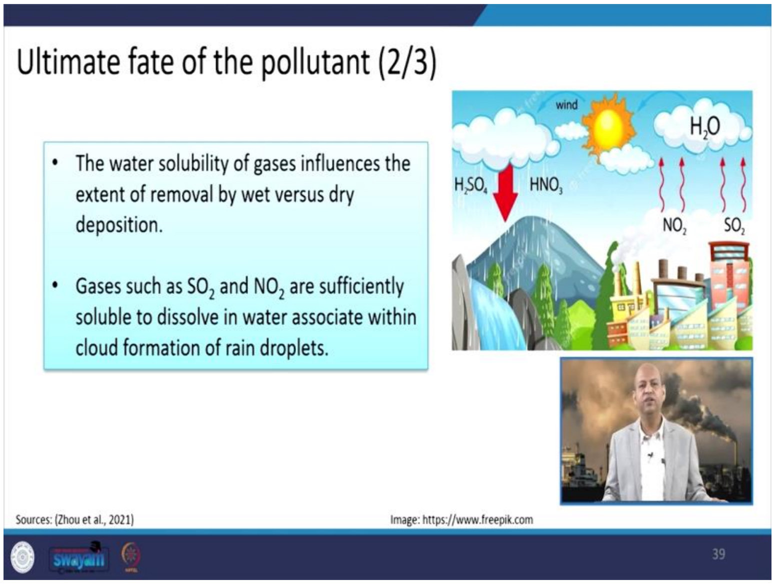
And then diffusion is basically the part of this, basically, this, when different molecules interact with each other and high concentration to low concentration movement is there. So that is the diffusion process of diluting of the concentrated pollutants.

(Refer Slide Time: 27:26)



Well, so ultimate fate of the pollutants are decided by these chemical transformations which we have seen, and physical transportation of the pollutants. So in this figure you can see for example, SO_2, NO_X is there, oxidation can happen, they can be part of the cloud formation, then dry deposition can also happen directly because of gravity and they, when they are part of the cloud formation, then precipitation can also happen. So this is the way it goes from one point to another.

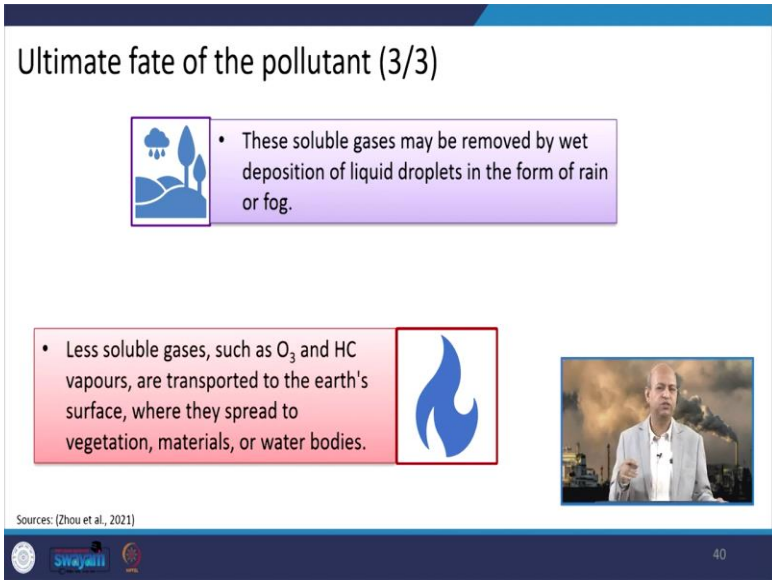
(Refer Slide Time: 27:58)



Similarly, the water solubility of gases, they also influence the extent of removal of wet versus dry deposition. How? Means, those are less soluble, they will deposit, they will get deposited dry otherwise they will convert it into some liquid phase and they will get, through precipitation or wet deposition.

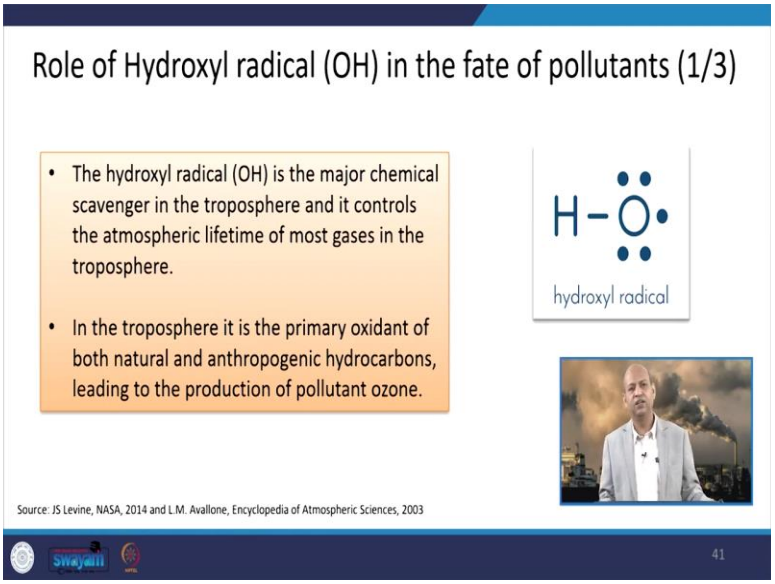
So SO_2, NO_2, they are basically soluble into the water. That is why they become part of the rain droplets and they cause the acid rain.

(Refer Slide Time: 28:33)



Then, we see about these soluble gases. They are removed by wet position, liquid droplets. And also there are like other gases which are not soluble, like ozone or hydrocarbons, vapors etc. And then some aerosols are also, so they go directly with the gravity and get deposited on plants, building surfaces etc, and they descends to the surface.

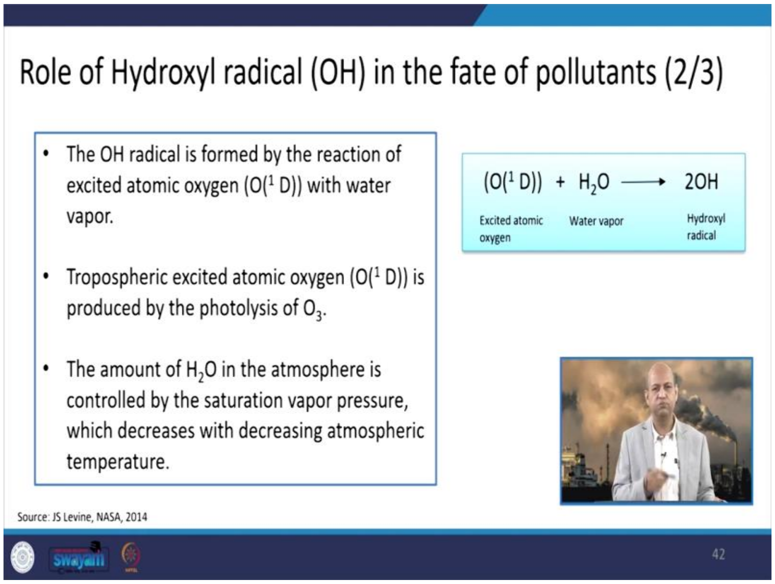
(Refer Slide Time: 29:01)



Well, there is this role, if you recall, I just explained a little about this hydroxyl radicals. Basically, they are the cleaning agent in the atmosphere. If there are no hydroxyl radicals and their lifetime is very, very small, but they are highly oxidising agents, they clean the atmosphere. And in tropical areas basically, this hydroxyl radicals concentration or production is very high.

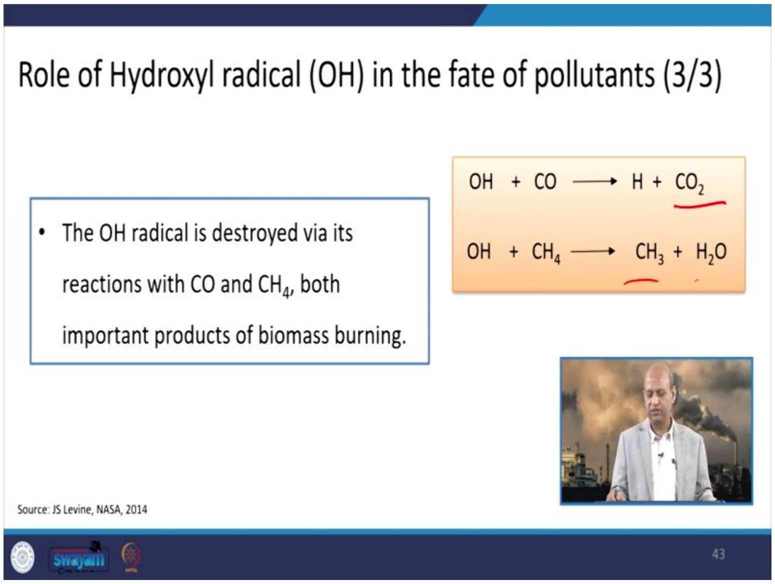
So that is why some atmospheric scientists say that those developed countries like Europe etc, they produce a lot of pollution and ultimately, because of global circulation, this pollution transports to those areas where equator is there, and there these, these hydroxyl radicals, they clean them. So this is known as, like a washing machine of the, the whole global atmosphere, this particular region.

(Refer Slide Time: 30:00)



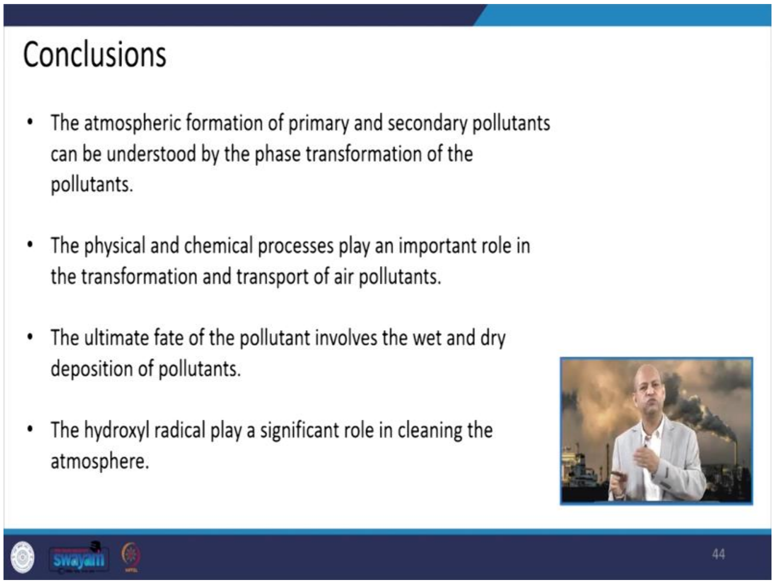
So you can see these hydroxyl radicals. They take part into the cleaning of the atom, these, because they oxidize many pollutants, and the self cleansing capacity is decided by these particular radicals.

(Refer Slide Time: 30:10)



You can see here, the CO, CH_4, all these can get converted into like CO_2 and CH_3, H_2O, those kind of conversion is there because of hydroxyl radicals.

(Refer Slide Time: 30:20)



So in conclusion, we can say that the atmosphere is responsible formation of secondary pollutants and there is, like phase transformation is there, that also plays a significant role. And then physical chemical processes are also there, they play an important role in transformation on transportation of air pollutants from one place to another.

And ultimate fate of the pollutant basically involves the dry and wet deposition of the pollutants. And the hydroxyl radicals play a very significant role in cleaning the atmosphere. So this is all for today. You might be now understanding how these atmospheric formation, transformation takes place, and then ultimate fate of the pollutants, what happens because of these reactions, chemical reactions which are happening in the atmosphere constantly. So this is all for today. Thank you for your kind attention.

(Refer Slide Time: 31:16)

These are the references for additional information. See you in the next lecture. Thanks again.