

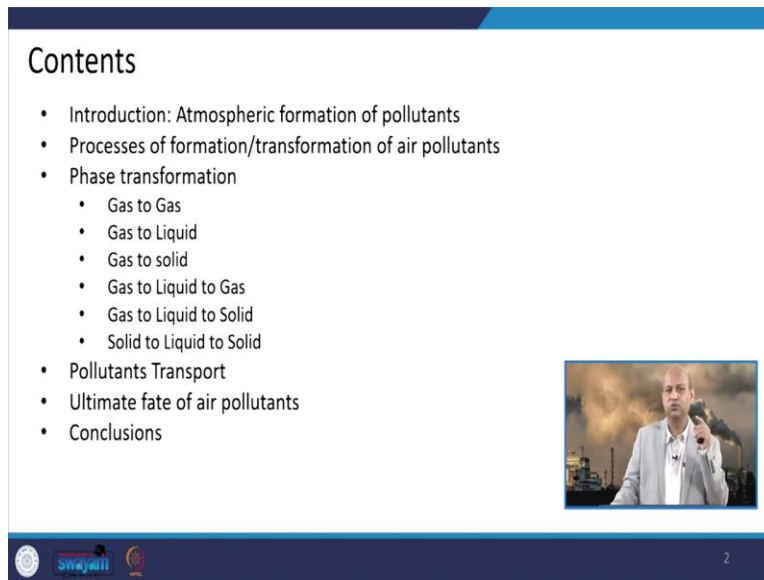
**Air Pollution and Control**  
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**Lecture 08**  
**Atmospheric Formation and Fate of Air Pollutants**

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.

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The slide is titled "Contents" and lists the following topics:

- Introduction: Atmospheric formation of pollutants
- Processes of formation/transformation of air pollutants
- Phase transformation
  - Gas to Gas
  - Gas to Liquid
  - Gas to solid
  - Gas to Liquid to Gas
  - Gas to Liquid to Solid
  - Solid to Liquid to Solid
- Pollutants Transport
- Ultimate fate of air pollutants
- Conclusions

At the bottom right of the slide, there is a small inset image of a man in a white shirt speaking into a microphone. The slide also features a blue header and footer with logos and the number "2".

So, in that framework we will see the phase transformation, like gas to gas, means, another gas like CO can get converted into CO<sub>2</sub>. Then gas to liquid. So, for example, SO<sub>2</sub> can get converted into H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, like that. Then gas to solid means, like calcium sulphate is formed in the presence of calcium particles and SO<sub>2</sub>, 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.

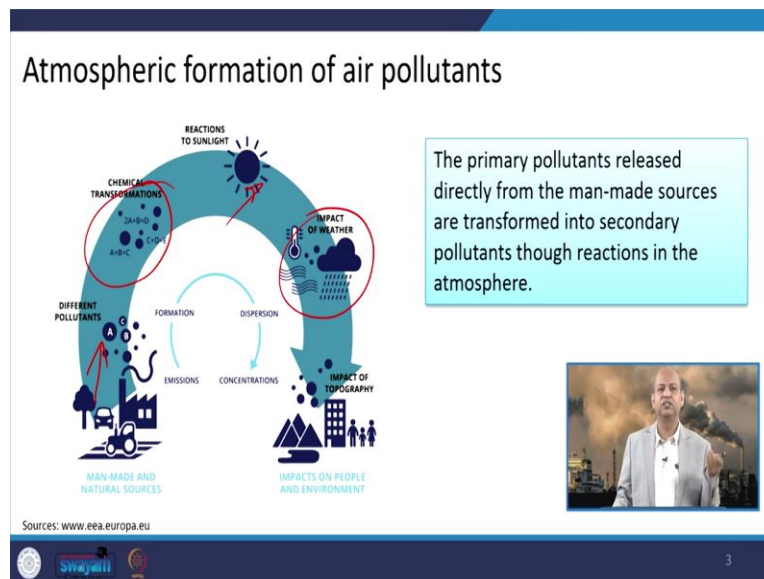
Then pollutants also transport. So, transformation and transportation, both things happen. From the source to the receptor, as I said, when it is emitted, pollutants are emitted, so, they will be transformed into something. When they reach to the destination, in between they will be transformed into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

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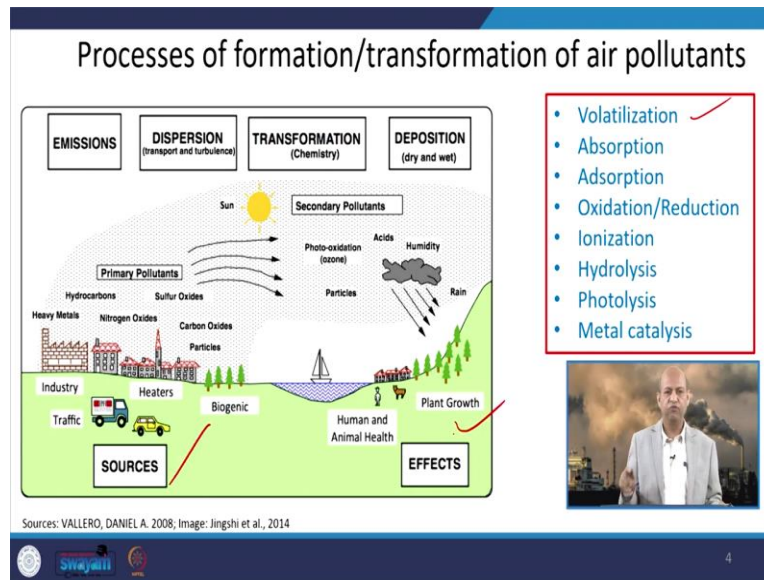


So, let's start. Like atmospheric formation of air pollutants. So, here it is shown that different pollutants are being emitted from various anthropogenic activities. Then chemical transformation is happening in the atmosphere. And in the presence of the sunlight, some photochemical reactions may also 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 come 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.

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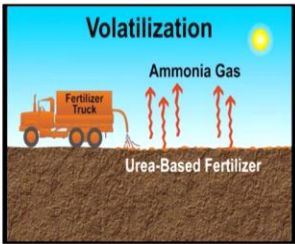
Well, so, the processes of formation and transformation of air pollutants can be listed like volatilization, absorption, adsorption, oxidation/reduction process, ionization or hydrolysis or photolysis or metal catalysis, all these things happen in the atmosphere. So, we will see those processes.

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.

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### Volatilization

- Volatilization is the conversion of a liquid chemical into a vapor, which escapes into the atmosphere.
- Mechanism : Physical



Sources: Ecotoxicological Testing, Scheunert, I., 1993, Image: <https://water.unl.edu>

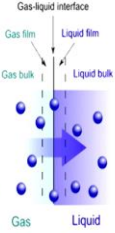
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So now, we see the volatilization. In this process basically the conversion of a liquid chemical into vapor because of this temperature and pressure, those physical processes there. So volatile compounds are there. You might have heard VOCs, Volatile 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.

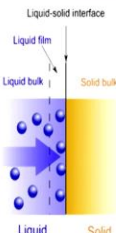
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### Absorption and Adsorption

**Absorption:** Transfer of a gaseous pollutant from the air into a contacting liquid, such as water.  
Mechanism : Chemical and physical.



**Adsorption:** Contaminates retention on solid particles presents in ambient air.  
Mechanism : Chemical and physical.



Sources: <https://www.britannica.com>, 14 Oct 2021, Image: [www.diffen.com](http://www.diffen.com)

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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<sub>2</sub> get converted into H<sub>2</sub>SO<sub>3</sub> 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.

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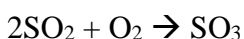
**Oxidation/Reduction**

- Oxidation: Electron loss
- Reduction: Electron gain.
- Mechanism: Chemical, physical

$$\begin{array}{c}
 \begin{array}{ccc}
 & \begin{array}{c} +2 \\ \text{Electron gain} \end{array} & \\
 \begin{array}{c} (+4) \quad (0) \\ 2 \text{SO}_2 + \text{O}_2 \end{array} & \longrightarrow & \begin{array}{c} (+6) \quad (-2) \\ \text{SO}_3 \end{array} \\
 \begin{array}{c} \text{Sulfur dioxide} \quad \text{Oxygen} \end{array} & & \begin{array}{c} \text{Sulfur trioxide} \end{array} \\
 & \begin{array}{c} -2 \\ \text{Electron loss} \end{array} & 
 \end{array}
 \end{array}$$


Sources: Doerr, Robert C., 1961, www.chemistrylearner.com

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<sub>2</sub>, this is giving these electrons and then this electron loss is there of minus 2 and SO<sub>3</sub> formation is there.

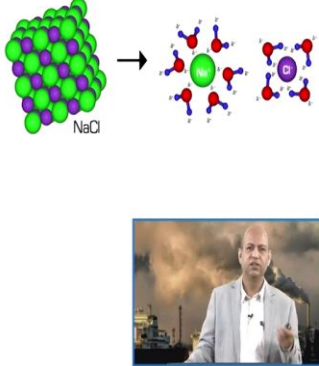


So that way you can see this oxidation and reduction process in this particular reaction or equation.

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## Ionization

- Complete co-solvation leading to separation of compound into **cations** and **anions**.
- Example: Dissolution of salts into ions.
- Mechanism : Chemical



Sources: VALLERO, DANIEL A. 2008  
Image: <https://www.visionlearning.com>

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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,  $\text{Na}^+$ ,  $\text{Cl}^-$ , 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  $\text{Na}^+$ ,  $\text{Cl}^-$ .

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### Hydrolysis

- Reaction of water molecules with contaminants.
- Mechanism : Chemical.

Sources: Rahm, Sara, et al., 2005      Image: <https://biology-igcse.weebly.com>

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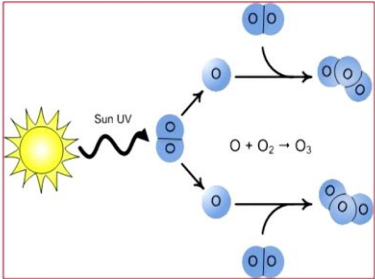
So, after ionization, we discuss about hydrolysis. In hydrolysis, like this  $\text{SO}_2$  goes into the atmosphere in the presence of  $\text{H}_2\text{O}$ , this becomes part of like, reaction of producing  $\text{H}_2\text{SO}_3$ , then  $\text{H}_2\text{SO}_4$ . Similarly,  $\text{NO}_x$  or  $\text{NO}_2$ , they get converted into  $\text{HNO}_3$  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.




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### Photolysis



Reaction catalyzed by electromagnetic (EM) energy (sunlight).

Mechanism : Chemical, physical



Sources: VALLERO, DANIEL A. 2008      Image: <https://sscchemistry.weebly.com>


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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.

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### Metal catalysis

- Reactions speed up in the presence of certain metallic compounds.
- Example:  $O_2$  and  $NH_3$  at  $850^\circ C$  and 5 atmospheres pressure, with the help of **Platinum and Rhodium catalysts**, to make  $NO$ . This is then oxidised to  $NO_2$ , which is then dissolved in water to make  $HNO_3$
- Mechanism : Chemical

$$4NH_3 + O_2 \rightleftharpoons 4NO + 6H_2O$$
$$2NO + O_2 \rightleftharpoons 2NO_2$$
$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$


Sources: VALLERO, DANIEL A. 2008      Image: <https://www.chemcool.com>

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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  $850^\circ C$  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.



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### Complete combustion

- Combustion is the combination of  $O_2$  in the presence of heat ( $\Delta$ ) (as in burning of fuel), producing  $CO_2$  and  $H_2O$  during complete combustion of organic compounds, such as the combustion of octane:

$$C_8H_{18} (l) + 17O_2 (g) \xrightarrow{\Delta} 8CO_2 (g) + 9H_2O (g)$$

Octane



Sources: VALLERO, DANIEL A. 2008

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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.

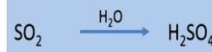
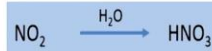
So that is why we talk that we should go for carbon neutral fuels so that extra  $CO_2$  is not dumped into the, or emitted into the atmosphere because that caused this global warming, climate change related issues. So the complete combustion from air pollutants point of view, it is fine because in complete 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.

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## Heterogeneous Reactions

- Heterogeneous reactions are defined as those involving the **gas-liquid or gas-solid phases**.
- The chemistry of  $\text{NO}_2$  and  $\text{SO}_2$  has a heterogeneous component in the atmosphere.
- The heterogeneous oxidation of  $\text{SO}_2$  in liquid droplets and water films is also a major pathway for conversion to sulfate in wet plumes and during humid or foggy conditions.



Sources: <https://www.britannica.com>, 14 Oct 2021

Image: <https://www.pinterest.com>


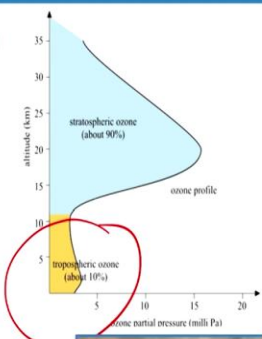


Then there is, there is this heterogeneous reactions are also there, like gas to liquid, gas solid phase, those kind of reactions maybe there. Like  $\text{NO}_2$ ,  $\text{SO}_2$ , they get converted into  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . So these are heterogeneous reactions which also happen in the atmosphere. So three reactions may happen, complete combustion, so those greenhouse gases  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  etc, or incomplete combustion, then of course, certain pollutants and these heterogeneous reactions can get phase transformation from gas to liquid or so.

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### Phase transformation: Gas to Gas (1/6)

- Ozone ( $O_3$ ) is constantly produced and destroyed in a natural cycle.
- Ozone is formed from a single recombination reaction of an **atomic oxygen and a molecular oxygen in the presence of a third body M**, which is required to carry away the energy released in the reaction (M is usually  $O_2$  or  $N_2$ ):

$$O + O_2 + M \rightarrow O_3 + M$$


Source: Atmospheric Chemistry, István Lagzi et al., 2013

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.

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Phase transformation: Gas to Gas (2/6)

- In the troposphere, **nitrogen dioxide** is the only known compound that can produce **Oxygen atom** during its photodissociation at available radiation.
- In the presence of NO, **O<sub>3</sub>** reacts with it, which reaction destroys the ozone and reproduces the **NO<sub>2</sub>**

$$\text{NO}_2 + h\nu (\lambda < 420\text{nm}) \rightarrow \text{O} + \text{NO}$$

$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$

$$\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$$



Source: Atmospheric Chemistry, István Lagzi et al., 2013

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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<sub>2</sub> from NO<sub>2</sub>, it can be there.


Then this O is available for reaction with this O<sub>2</sub>. So ozone is produced. And O<sub>2</sub>, this ozone can react with NO and produce NO<sub>2</sub> 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<sub>2</sub> goes in the downwind direction in the countryside with a lot of sunshine is there. So in countryside or rural areas, this NO<sub>2</sub> will produce again ozone by this kind of reaction. So that is very interesting thing, you should remember.

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### Phase transformation: Gas to Gas (3/6)

- Ozone molecule absorbs solar radiation and decomposes back to  $O_2$  and  $O$ .
- Because the bonds in the  $O_3$  molecule are weaker (364 KJ/mol) than those in the  $O_2$  molecule, photolysis is achieved with lower-energy photons (in the wavelength range of 240 to 320 nm):

$$O_3 + h\nu (\lambda < 320\text{nm}) \rightarrow O_2 + O$$


Source: Atmospheric Chemistry, István Lagzi et al., 2013

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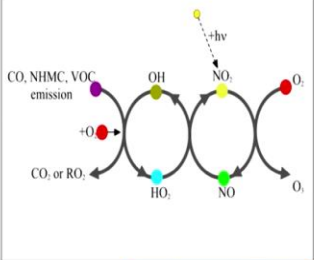
Now, this, this ozone molecule absorbs solar radiation and it can also get decomposed back to Oxygen. So this kind of reaction can happen.

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### Phase transformation: Gas to Gas (4/6)

➤ Ozone ( $O_3$ ) formation in atmosphere 2/2

- Net ozone production occurs, when other precursors, such as carbon monoxide ( $CO$ ), methane ( $CH_4$ ), non-methane hydrocarbons (NMHC) or certain other organic compounds (volatile organic compounds – VOC) are present in the atmosphere.



Source: Atmospheric Chemistry, István Lagzi et al., 2013

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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  $\text{NO}_x$ , 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.

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Phase transformation: Gas to Gas (5/6)

### Tropospheric Ozone

**Ozone from  $\text{NO}_x$**   
 $\text{NO}_x + \text{radiations } (>380 \text{ nm}) \longrightarrow \text{NO} + \text{O}$   
 $\text{O} + \text{O}_2 \longrightarrow \text{O}_3$

**Ozone from carbon monoxide**  
 $\text{CO} + 2\text{O}_2 + h\nu \longrightarrow \text{CO}_2 + \text{O}_3$

**Ozone from methane**  
 $\text{CH}_4 + 4\text{O}_2 + 2h\nu \longrightarrow \text{HCHO} + \text{H}_2\text{O} + 2\text{O}_3$   
 $\text{HCHO} + h\nu \longrightarrow \text{H} + \text{HCO} (\lambda < 330 \text{ nm})$   
 $\text{HCO} + h\nu \longrightarrow \text{H} + \text{CO} (\lambda < 360 \text{ nm})$   
 $\text{CO} + 2\text{O}_2 + h\nu \longrightarrow \text{CO}_2 + \text{O}_3$

**Ozone from non methane hydrocarbons**  
 $\text{RH} + 4\text{O}_2 + 2h\nu \longrightarrow \text{RCHO} + \text{H}_2\text{O} + 2\text{O}_3$

Volatile Organic Compounds (VOCs) + Nitrogen Oxides ( $\text{NO}_x$ ) + sunlight  $\longrightarrow$  ground level ozone

- The role of **VOCs / hydrocarbons (HCs)** along with  **$\text{NO}_x$**  in the formation of **Ozone**.

Sources: RAI, 2019  
 Image: <https://butane.chem.uiuc.edu>

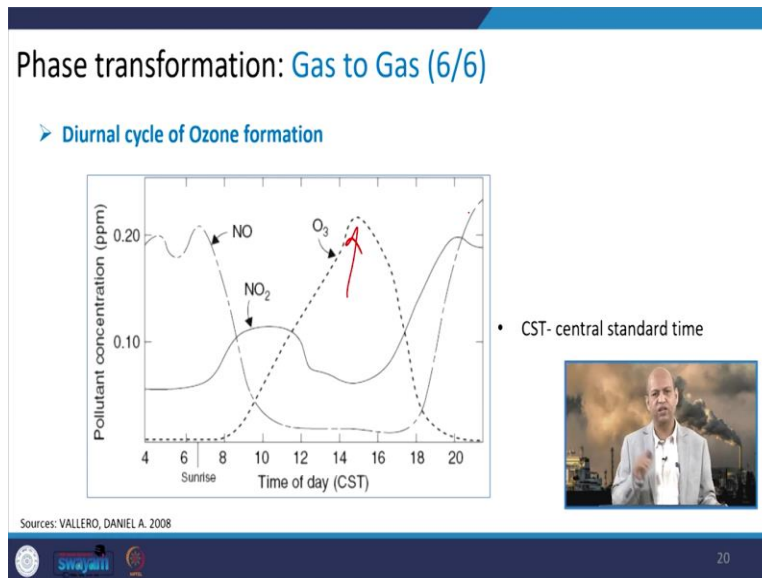
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So ultimately this gas to gas transformation can be nicely depicted in this particular set of reactions, where  $\text{NO}_x$  is converted into NO and O, and ozone is produced, CO also gives the like  $\text{CO}_2$  and this ozone, and this methane 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  $\text{NO}_x$  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.



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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  $\text{NO}_2$  production. Then in the sunlight a lot of this ozone production is there, but  $\text{NO}_2$  is consumed in the production of ozone. So  $\text{NO}_2$  is less here.

Then again ozone diminishes in the evening time and this NO starts to increase, and this  $\text{NO}_2$  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  $\text{NO}_x$  relationship in the urban areas.

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### Phase transformation: Gas to Liquid (1/4)

• Atmospheric chemical transformations are classified in terms of whether they occur as a gas, on a surface, or in a liquid droplet.

• For example: The oxidation of dissolved  $\text{SO}_2$  in a liquid droplet.

Sources: VALLERO, DANIEL A. 2008 Image: <https://www.degruyter.com>

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Well, the phase transformation, now we go for gas to liquid. You can see here like gas,  $\text{SO}_2$  is there, and moisture is there. So then, in the presence of moisture it can get converted into  $\text{HSO}_3^-$ . Ultimately, it can get converted into  $\text{H}_2\text{SO}_4$ .

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### Phase transformation: Gas to Liquid (2/4)

•  $\text{H}_2\text{S}$  undergoes oxidation producing  $\text{SO}_2$  followed by oxidation of  $\text{SO}_2$  to sulphuric acid ( $\text{H}_2\text{SO}_4$  or  $\text{SO}_4^{2-}$ ).

$$\text{H}_2\text{S} + 2\text{O}_2 \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+$$

Source: Atmospheric Chemistry, István Lagzi et al., 2013


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So here, you can see this  $\text{H}_2\text{SO}_4$  production is shown in this figure as well as in, in this reaction.

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### Phase transformation: Gas to Liquid (3/4)

- Sulphur dioxide reacts with an OH radical.
- The HSO<sub>3</sub> radical then rapidly reacts with molecular oxygen to yield SO<sub>3</sub> and HO<sub>2</sub>
- The produced SO<sub>3</sub> reacts with water (catalyzed by another water molecule) to yield sulphuric acid.

$$\text{SO}_2 + \text{OH}^\bullet \rightarrow \text{HSO}_3^\bullet$$
$$\text{HSO}_3^\bullet + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2^\bullet$$
$$\text{SO}_3 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$$


Source: Atmospheric Chemistry, István Lagzi et al., 2013


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So this is the complete reaction, set of reactions where sulphur dioxide reacts with the OH radicals, hydroxyl radicals, and this HSO<sub>3</sub> radical then rapidly reacts with molecular oxygen to yield SO<sub>3</sub> and HO<sub>2</sub> and ultimately this sulfuric acid is produced.

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### Phase transformation: Gas to Liquid (4/4)

- NO<sub>2</sub> reacts with OH radical for the formation nitric acid.
- NO<sub>3</sub> is converted into nitric acid by reacting with the compound such as hydrocarbons and aldehydes.

$$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$$
$$\text{NO}_3 + \text{RH} \rightarrow \text{HNO}_3 + \text{R}$$


Source: Atmospheric Chemistry, István Lagzi et al., 2013


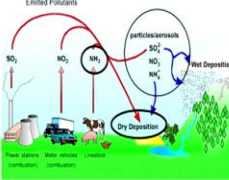
24

Well, similarly, NO<sub>2</sub> to get converted into HNO<sub>3</sub>. So this is the same gas to liquid transformation or phase transformation happens of the pollutants.

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### Phase transformation: Gas to Solid (1/2)

- In most of the regions impacted by human activities (e.g. agriculture and industry), emissions of ammonia (NH<sub>3</sub>) are prevalent.
- When a gas changes into a solid, it is called deposition.
- Ammonia is gas phase base, and can act to neutralize sulfate particles either partly or often completely by the formation of the ammonium (NH<sub>4</sub><sup>+</sup>) ion:

$$\text{H}_2\text{SO}_4(\text{gas}) + 2\text{NH}_3(\text{gas}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{particle})$$


Source: Geddes, J. A., & Murphy, J. G. (2012); Image: Air Pollution Information System, <http://www.apis.ac.uk/>

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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<sub>2</sub> 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)

### Phase transformation: Gas to Solid (2/2)

- Nitric acid in gas phase is mainly incorporated into particles only in the presence of ammonia.
- The formation of nitrate particles is dependent on the production rate of  $\text{HNO}_3$ , but is also very strongly related to the availability of ammonia.

$$\text{HNO}_3(\text{gas}) + \text{NH}_3(\text{gas}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{particle})$$

- This is because  $\text{H}_2\text{SO}_4$  being stronger acid outcompetes  $\text{HNO}_3$  for  $\text{NH}_3$  no matter how much  $\text{HNO}_3$  is available.
- Any leftover  $\text{NH}_3$  (or 'excess ammonia') can then be used to react with  $\text{HNO}_3$  and form  $\text{NH}_4\text{NO}_3$  particles.



Sources: VALLERO, DANIEL A. 2008

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Then, also, this  $\text{HNO}_3$  and ammonia, that is, ammonium nitrate, again, the particle. But this  $\text{H}_2\text{SO}_4$ , 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)

### Phase transformation: Gas to Liquid to Gas (1/2)

Gases

- $\text{NO}_2 + \text{Sunlight} \rightarrow \text{NO} + \text{O}$
- $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
- $\text{NO} + \text{VOC} \rightarrow \text{NO}_2$

Liquid

- $\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$


Formation of PAN

- $\text{NO}_2 + \text{VOC} \rightarrow \text{PAN (Peroxyacyl Nitrates)}$

Resultant reaction of Photochemical Smog

- $\text{NO} + \text{VOC} + \text{O}_2 + \text{Sunlight} \rightarrow \text{O}_3, \text{PAN, and other oxidants}$

- Solar radiation influences the chemical processes in the atmosphere by interacting with molecules that act as photo-acceptors.
- In photochemical smog, the principal photo-acceptors are VOCs,  $\text{NO}_2$ , nitric acid ( $\text{HNO}_3$ ), and ozone.



Sources: VALLERO, DANIEL A. 2008

27

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  $\text{NO}_2$  sunlight, is it dissociate into  $\text{NO}$  and  $\text{O}$  and available. So this react with the oxygen molecule and ozone is produced. And then VOC and  $\text{NO}$ , if it is there then  $\text{NO}_2$  is produced. And  $\text{NO}_2$  get converted into  $\text{HNO}_3$ . And  $\text{NO}_2$  can also produce, ultimately the ozone.

So the liquid, this  $\text{HNO}_3$ , this  $\text{NO}_2$  is taking part here with  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  is produced. So the first transformation from gas to liquid happening. Now you can see here, this is a  $\text{NO}_2$  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.

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Phase transformation: Gas to Liquid to Gas (2/2)

➤ Example: Formation of photochemical smog

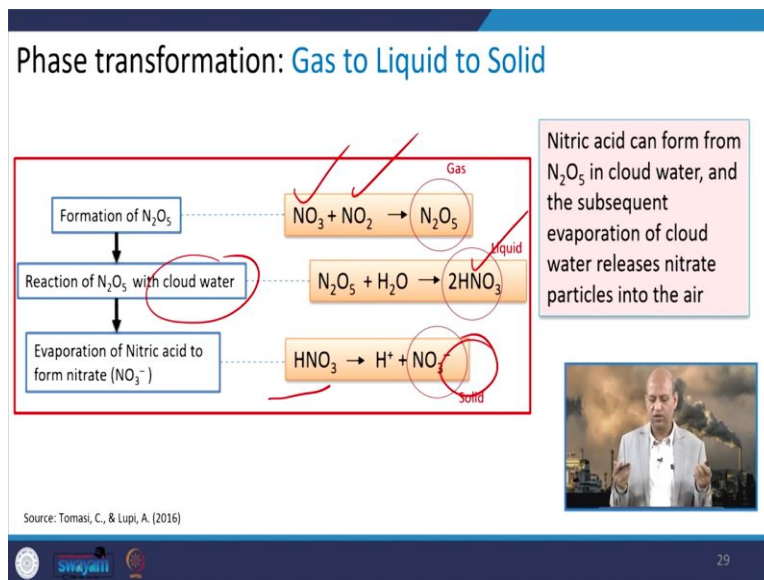
Sources: <https://energyeducation.ca>, 15 Oct 2021

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Now, again this pictorial representation is there. How this H<sub>2</sub>O, 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<sub>3</sub> 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.

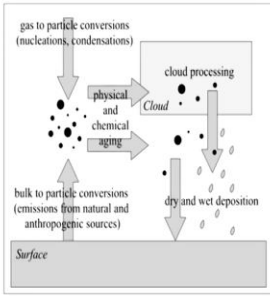
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Then gas to liquid to solid, that is another interesting part, you can see here. Like, this gas is produced, formation of N<sub>2</sub>O<sub>5</sub>. This is NO<sub>3</sub>, NO<sub>2</sub> all these gases. They get converted into gas. Then this reaction N<sub>2</sub>O<sub>5</sub>, with the cloud water, moisture, so N<sub>2</sub>O<sub>5</sub> plus H<sub>2</sub>O, it gives us HNO<sub>3</sub>, liquid transformation, from gas to liquid. Now, HNO<sub>3</sub> 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.


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### Phase transformation: Solid to Liquid to Solid (1/3)



The diagram illustrates the sources and sinks of aerosols. It shows a cycle starting from the 'Surface' where 'bulk to particle conversions (emissions from natural and anthropogenic sources)' occur. These particles undergo 'gas to particle conversions (nucleations, condensations)' and 'physical and chemical aging' in the 'Cloud'. 'cloud processing' leads to 'dry and wet deposition' back to the 'Surface'.

- **Aerosol** is a system of solid or liquid particles suspended by a mixture of gases.
- The term aerosols covers a wide spectrum of small particles, like sea salt particles, mineral dust, pollen, drops of sulphuric acid and many others.



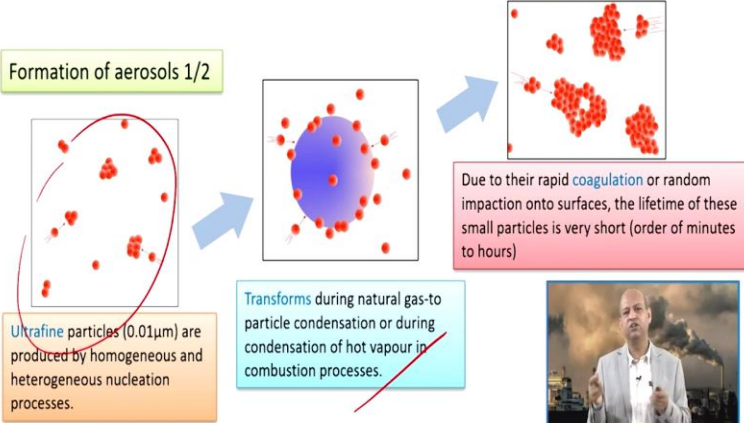
Source: Atmospheric Chemistry, István Lagzi et al., 2013

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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)

### Phase transformation: Solid to Liquid to Solid (2/3)



The diagram shows the formation of aerosols and their subsequent coagulation. It starts with 'Formation of aerosols 1/2' where 'Ultrafine particles (0.01µm) are produced by homogeneous and heterogeneous nucleation processes.' These particles 'Transforms during natural gas-to-particle condensation or during condensation of hot vapour in combustion processes.' The particles then undergo 'coagulation' or 'random impaction onto surfaces', leading to larger clusters. A text box notes: 'Due to their rapid coagulation or random impaction onto surfaces, the lifetime of these small particles is very short (order of minutes to hours)'. A video inset shows a speaker.

Source: Atmospheric Chemistry, István Lagzi et al., 2013

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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.


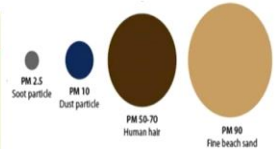
Then due to the rapid coagulation or random impaction onto the surface, the lifetime of these small particles is very short. So this solid to liquid to solid, this transformation happens very quickly and within hours these reactions are there.

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**Phase transformation: Solid to Liquid to Solid (3/3)**

Formation of aerosols 2/2

- Larger aerosol particles in the size range 0.1 to 1  $\mu\text{m}$  in diameter can accumulate in the atmosphere because their removal mechanisms are least efficient.
- Their lifetime in the atmosphere is 7–10 days and during this period they can be transported to a long distance from their sources.
- Particles belonging to this accumulation mode are formed mainly by coagulation.



Source: Atmospheric Chemistry, István Lagzi et al., 2013

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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)

### Pollutants Transport

The diagram illustrates the transport of pollutants from a source to three receptors. It shows the following processes: Emission from a source, buoyant plume, turbulence (eddy mixing), convection, advection by winds, clouds, and long-range transport. The receptors are labeled Source, Receptor-1, Receptor-2, and Receptor-3.

Transport is one of the two processes (the other is transformation) that determine a contaminant's fate in the environment.

- Advection
- Convection
- Dispersion
- Diffusion

Sources: VALLERO, DANIEL A. 2008; Image: <http://irina.eas.gatech.edu/>

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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.


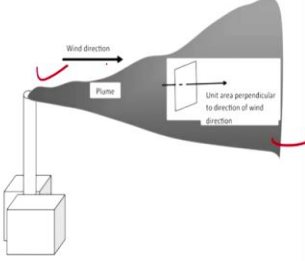
Because of convection, this temperature difference and pressure difference, the vertical movement is also there, which is known as the convection. And turbulence also helps in the dispersion and diffusion of the pollutants, and ultimately they become part of clouds and they come down with the precipitation.

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

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### Advection

- Change in a property of a moving mass of air because the mass is transported by the wind to a region where the property has a different value.
- Advection is responsible for horizontal transport of pollutants.



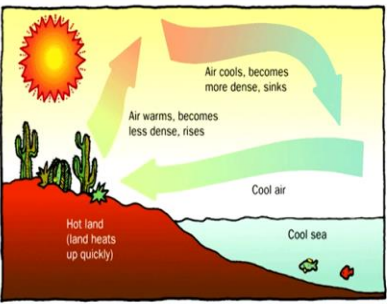
Sources: <https://www.britannica.com>, 14 Oct 2021 Image: VALLERO, DANIEL A. 2018

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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.


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### Convection



Convection is one of the processes of movement of gases and liquids (fluids) to transfer heat between regions of different temperatures.

It is responsible for vertical movement of air pollutants.



Source: VALLERO, DANIEL A. 2018 ;Image: [www.ausearthed.blogspot.com](http://www.ausearthed.blogspot.com)

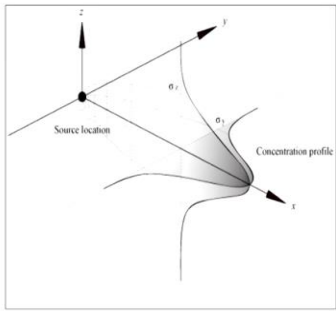
35

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.

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### Dispersion



- Pollutant dispersion is the transportation of aerial pollutants in the outdoor atmosphere after being emitted from the sources.
- Mechanism : Mechanical



Sources: VALLERO, DANIEL A. 2018 Image: <https://www.mdpi.com>


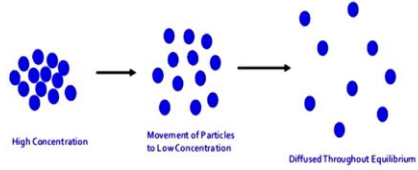
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Dispersion happens, because of this turbulence and then wind movement.

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### Diffusion

- ❖ Transport of air pollutants driven by concentration gradient (as per Fick's Law).
- ❖ Fick's Law : The movement of the gas will be proportional to the concentration gradient (higher concentration to lower concentration )



Sources: [Bekey et al., 1958] Image: <https://www.aplustopper.com/diffusion>

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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.

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### Ultimate fate of the pollutant (1/3)

• The removal of material from the atmosphere involves two processes: wet and dry deposition.

Sources: VALLERO, DANIEL A. 2008  
Image: <https://www.srs.fs.usda.gov>


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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,  $\text{SO}_2$ ,  $\text{NO}_x$  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.

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### Ultimate fate of the pollutant (2/3)

- The water solubility of gases influences the extent of removal by wet versus dry deposition.
- Gases such as  $\text{SO}_2$  and  $\text{NO}_2$  are sufficiently soluble to dissolve in water associate within cloud formation of rain droplets.



Sources: (Zhou et al., 2021) Image: <https://www.freepik.com>

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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  $\text{SO}_2$ ,  $\text{NO}_2$ , they are basically soluble into the water. That is why they become part of the rain droplets and they cause the acid rain.

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### Ultimate fate of the pollutant (3/3)

- These soluble gases may be removed by wet deposition of liquid droplets in the form of rain or fog.
- Less soluble gases, such as  $O_3$  and HC vapours, are transported to the earth's surface, where they spread to vegetation, materials, or water bodies.



Sources: (Zhou et al., 2021)


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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.


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### Role of Hydroxyl radical (OH) in the fate of pollutants (1/3)

- The hydroxyl radical (OH) is the major chemical scavenger in the troposphere and it controls the atmospheric lifetime of most gases in the troposphere.
- In the troposphere it is the primary oxidant of both natural and anthropogenic hydrocarbons, leading to the production of pollutant ozone.



hydroxyl radical



Source: JS Levine, NASA, 2014 and L.M. Avallone, Encyclopedia of Atmospheric Sciences, 2003

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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.




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### Role of Hydroxyl radical (OH) in the fate of pollutants (2/3)

- The OH radical is formed by the reaction of excited atomic oxygen ( $O(^1D)$ ) with water vapor.
- Tropospheric excited atomic oxygen ( $O(^1D)$ ) is produced by the photolysis of  $O_3$ .
- The amount of  $H_2O$  in the atmosphere is controlled by the saturation vapor pressure, which decreases with decreasing atmospheric temperature.

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

Excited atomic oxygen      Water vapor      Hydroxyl radical



Source: JS Levine, NASA, 2014


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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.

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### Role of Hydroxyl radical (OH) in the fate of pollutants (3/3)

- The OH radical is destroyed via its reactions with CO and  $CH_4$ , both important products of biomass burning.

$$OH + CO \longrightarrow H + CO_2$$
$$OH + CH_4 \longrightarrow CH_3 + H_2O$$


Source: JS Levine, NASA, 2014


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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.

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## Conclusions

- The atmospheric formation of primary and secondary pollutants can be understood by the phase transformation of the pollutants.
- The physical and chemical processes play an important role in the transformation and transport of air pollutants.
- The ultimate fate of the pollutant involves the wet and dry deposition of pollutants.
- The hydroxyl radical play a significant role in cleaning the atmosphere.



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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)

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