Environmental Air Pollution

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Lecture No. 10
Kinetics of Air Pollution and Combustion Processes

I want you to be very very thorough with how ozone is being formed and what are the responsible radicals, how they react and how the HO_2 is produced and how HO_2 can transfer the NO into NO_2. If you, we were doing the chemistry of methane. It can in fact remove NO_2 from the system rather than forming NO_2. Once we are able to form the NO_2, then we are likely to form the ozone and if NO_2 becomes too much, then what happens? The NO_2 will go to the terminal reaction and form more of HNO_3, right? That is how it gets out of the system – the HNO_3. Maybe we will discuss a little later but you should also not forget that life does not end with forming HNO_3.

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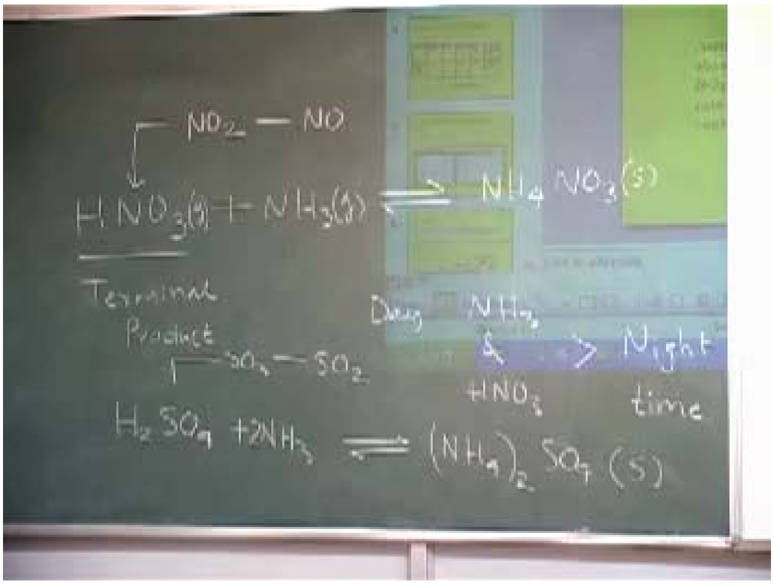

This was the terminal product but we all know acid itself is highly reactive. The moment it encounters ammonia, which is there a lot in the atmosphere, we are doing some measurements of ammonia and maybe we will talk about [01:59]….Then, you will find…. Is it balanced? N, H, 4, NH_4NO_3. You started with ammonium nitrate. What is it? It is a salt. This comes as a [02:31] heterogeneous equation. It is a solid and it makes very fine particles.

We thought that the problem of the particles is over, but you see that particles will be found because of the primary gases that you have in the form of gas here. [02:53] and if the temperatures are very high, then what can happen is this is a reversible reaction and you can also form back the ammonia and HNO_3.

During daytime, you will find NH_3 and HNO_3, generally, larger than nighttime. Both will be high because of the volatility. Normally, this will be the situation but NH_4NO_3 itself is volatile – you know about ammonium nitrate. If the temperatures are high, you can see that the NH_4NO_3 is evaporated and you do not find the particles. In the same gas chamber, you can see that for a moment, there is nothing – all gaseous compounds, but after some time, no reaction is happening, the temperature drops and you can see the particles. This is the situation.

We have not discussed the end product so much. This is the terminal reaction for SO_2 or H_2SO_4 plus ammonia produces $(NH_4)_2SO_4$ and then of course you have to balance the equation. How do I balance? 2 nitrogen, 1 nitrogen, 2 nitrogen, 6 plus 2 – 8 hydrogen, 8 hydrogen and this sulfate is sulfate. You get it without any problem. Again, these are…. We have the serious problem of dust in the country. Where is the dust coming from? It is not only the natural dust that comes. The primary origin of these particles, which we call in a broad sense as dust, has come from…. Where has this NO_3 come from? It has come from NO_2, and this has come from NO and this has come from SO_3 and SO_2.

Where do we make these particles responsible? They are responsible from the combustion sources. It is very important to understand that if you want to control the emissions or we want to improve the air quality in terms of the particles, in terms of the dust, it is just not the particles that you control at the power plant but you also need to control the gases that eventually form ammonium nitrate and ammonium sulfate in the atmosphere. We have to do some work on that but what we will do is maybe we will discuss a little bit more about those things at some point.

Let us get back to something that that we were doing in the last class. I thought it might be a good idea to do a simple example that I was just emphasizing on – you should learn to do these problems as you see them. You can take this as an assignment. I have done almost 80 percent. You can take that as an assignment or an example.

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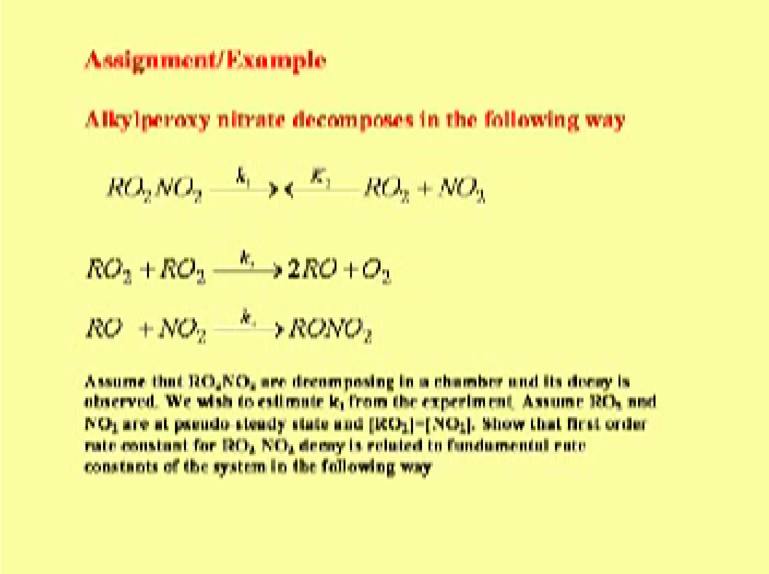

Assignment/Example

Alkylperoxy nitrate decomposes in the following way

$$RO_2NO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} RO_2 + NO_2$$

$$RO_2 + RO_2 \xrightarrow{k_3} 2RO + O_2$$

$$RO + NO_2 \xrightarrow{k_4} RONO_2$$

Assume that RO_2NO_2 are decomposing in a chamber and its decay is observed. We wish to estimate k_1 from the experiment. Assume RO_2 and NO_2 are at pseudo steady state and $[RO_2]=[NO_2]$. Show that first order rate constant for RO_2 NO_2 decay is related to fundamental rate constants of the system in the following way

I am talking arbitrarily about an alkyl that is for these [07:06] for R. Alkyl peroxy nitrate decomposes [07:11] the peroxy oxides, peroxy radicals. What you can see is that this is a two-way reaction. In the forward direction, I am calling that as k_1 and the backward I am calling as k_2. It breaks down into RO_2 and NO_2. This RO_2 and RO_2 can combine to produce 2 RO and oxygen. These are all radicals; you should see a little dot here, a dot there, a dot there and the dot here.

The RO can further decompose or rather react with NO_2 to produce $RONO_2$, not RO_2NO_2 but $RONO_2$. How are we finding the rate constant and rate reactions for this? There is a little example. Just assume that RO_2NO_2 (there could be many compounds like this) is decomposing in a chamber. I do more like a batch study, put everything in the chamber, put the sensors, and continuously measure the concentration with respect to time. We are observing the decomposition of RO_2NO_2 and the idea is that we want to estimate k_1 from the experiment – that is what we are doing.

You can also assume that RO_2 and NO_2 are at pseudo-steady state. Now, you have to explain to me the meaning of pseudo-steady state. We have done many problems in the class and we have discussed what pseudo-steady state condition is. Many times even if it is not a steady state, we somehow assume it to be pseudo-steady state provided it matches with certain conditions. Now, you tell me what pseudo-steady state is because this kind of assumption, this kind of understanding will be required in many problems that you do. Pseudo-steady state. One thing is certain – it is not steady state. What is pseudo-steady state then? Try.

[Conversation between student and professor - Not Audible (09:27 min)]

Yes. What it really implies is that it is not for short time. What it says is that whatever you are putting at steady state, its rate of decomposition or rate of degeneration is the same – approximately. What you are saying is the derivative of these compounds or these radicals or these species with respect to time can be taken as approximately equal to 0 because we are saying that these things are not changing their type – they are constantly generated and constantly degenerated.

We can say that this will be at the pseudo-steady state and the second assumption, which is not such a bad assumption if you know the theory, is that the molar quantity of these two is the same. Now what we do with this is show that the first-order rate constant decay of this is related to the fundamental rate constants of the system in the following way. What are the fundamental rate constant of system? k_2 k_3 k_4.

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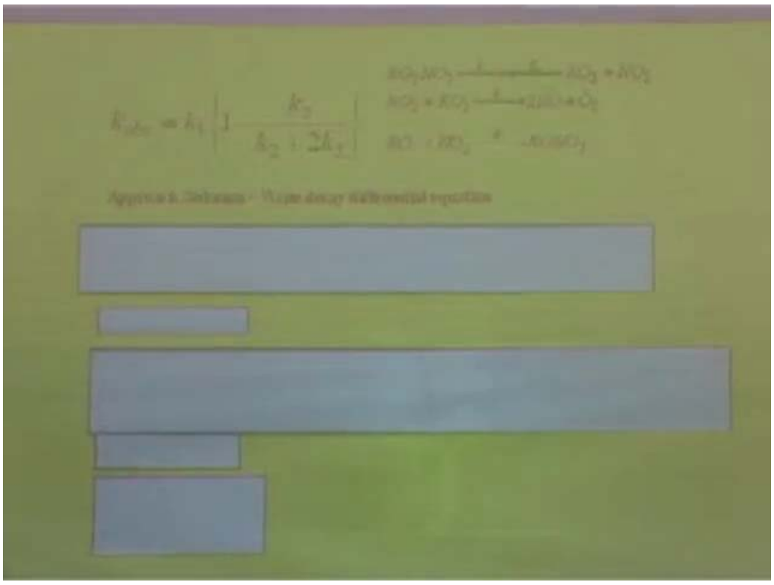

Those are the reactions, I write them back for you. The k you are observing are related with this. What do you mean by observing the k? What I am really observing in my reaction is time.

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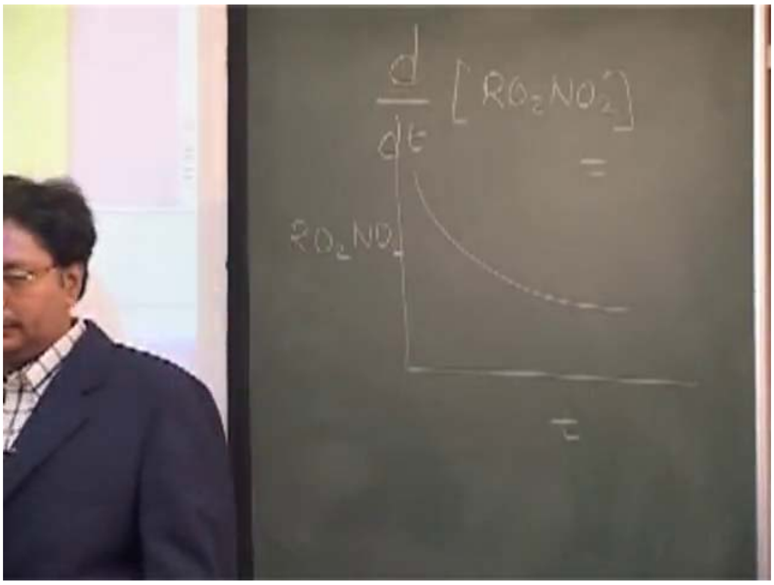

I am just measuring RO_2NO_2 [11:18] some time left and then I am finding something like this – some kind of decay. Will it depend fully on k_1 only? It will not depend on k_1 alone. Why not k_1? It is because this is also a reversible reaction and it can also depend on the quantity of RO_2. RO_2 depends on this reaction (Refer Slide Time: 11:50) and this depends on this. All the equations are interlinked. I cannot talk about one thing in isolation and say that I can find out straightaway the rate constant of this. k_1 is separate but what I am observing here is separate. That is the important thing that you need to realize.

Is this equal to k_1? No. I can find out the slope – I am sure you must have done dc by dt equals to minus k c. I can just write dc by dt equals to minus k c and find the k. That k is not equal to k_1 but it is a combination of k_1, k_2 and k_3. What is that combination? That is what you have to derive. I have done this to a large extent. I want you to write the differential equation for the decay of RO_2NO_2. Why do you not try that quickly and see if that matches with the answer that I have, so that you get used to writing? We do not give as many assignments as we should. So maybe you should try and see if you get the same equation as what I am getting. Try quickly. You know I cannot give you so much of time.

The reactions are there. I want to write d by dt of RO_2NO_2. I am sure all of you must have done this, so let us open the box. Here you go. Have I done a reasonable job or is there an error? There is no error. Just make sure that you understand what I have written and why I have written.

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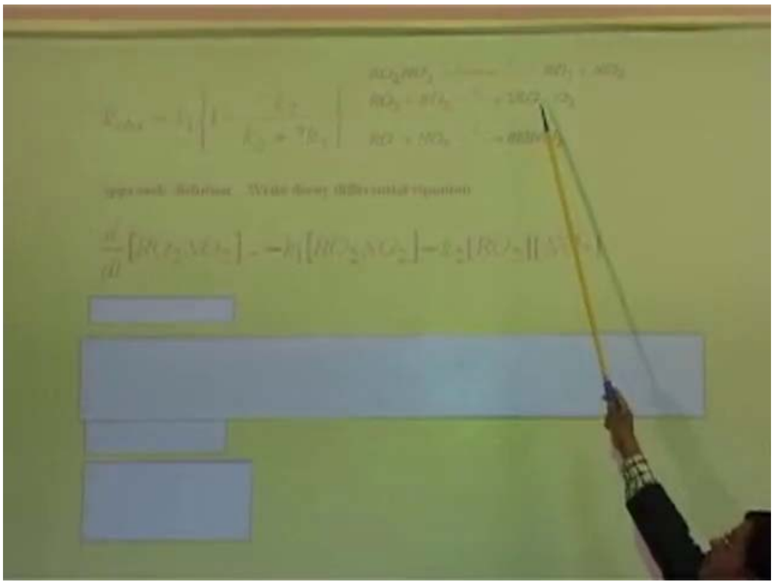

The decomposition of RO_2 depends only on what is the concentration of RO_2NO_2 because the reaction in the reversible direction is possible – so that of RO_2 and NO_2.

[Conversation between student and professor - Not Audible (14:41 min)]

All right, all right, take that as plus k_2 – I agree with you. You should take that as plus k_2. If that is done, let us go forward and see.

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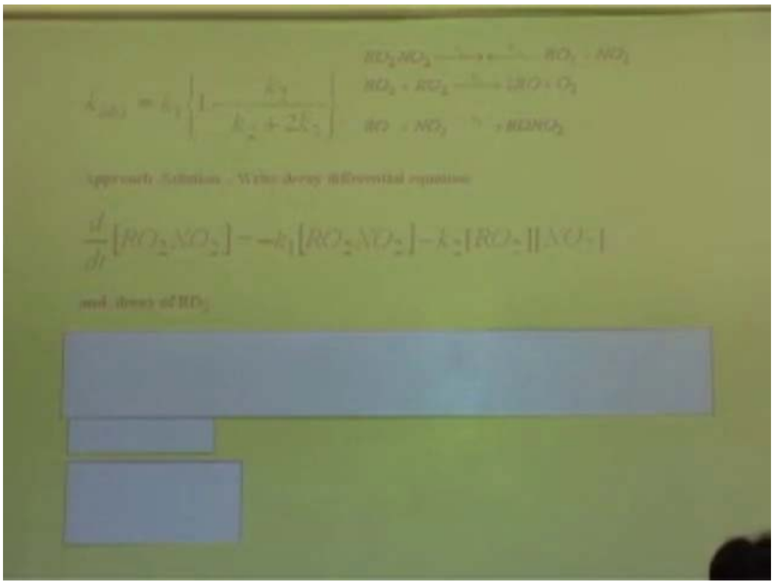

Decay of RO_2. Do you want to write the equation for RO_2? I am sure you have all done that.

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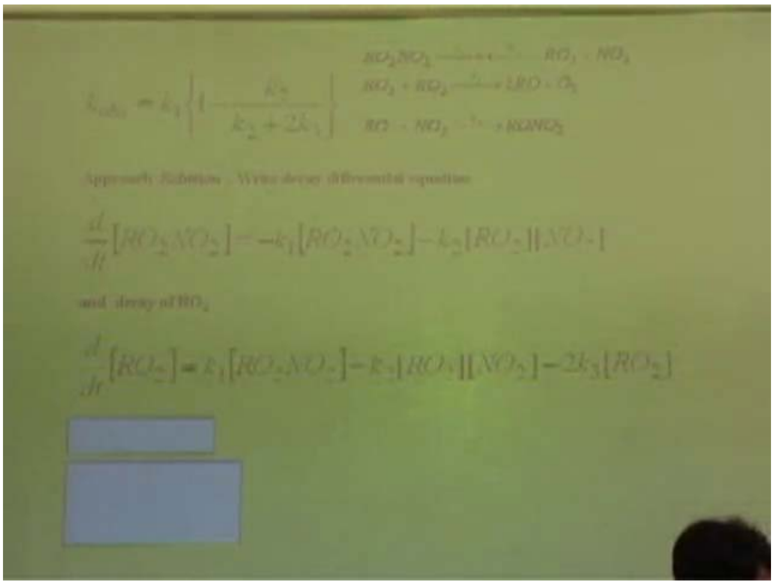

Make sure this is correct. Possibly, there is an error too but you should see that this is okay. Now, we are talking about the decomposition of RO_2. That will depend on k_1 – sure, that will also will depend on k_2 with negative sign and that will also depend on k… what should I say here? There is a square here (Refer Slide Time: 15:45). There has to be square but that is not coming up here. This looks all right. We have written this equation, we have written this equation and I am just wondering if there is anything missing. k_1 is fine. k_1 will be plus for RO_2, RO_2 disappears through k_2 because of this, k_3 is again decomposing RO_2 and that is all, right? Very good. Then, what we need to do is something very simple.

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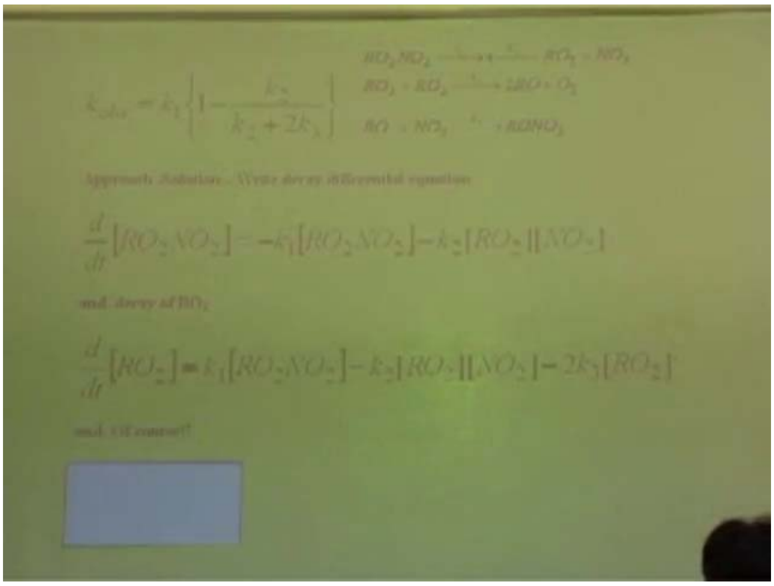

And of course. What else? What will be this derivative equal to? 0.

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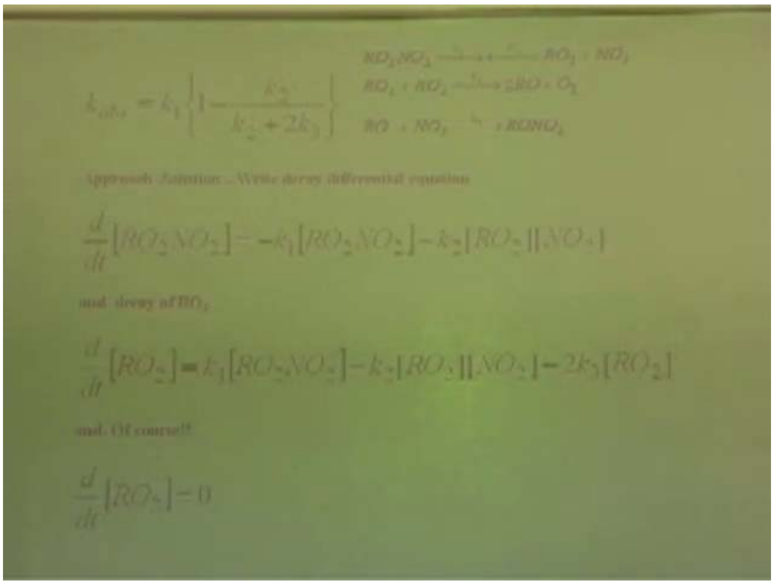

$$k_{obs} = k_1\left\{1-\frac{k_2}{k_2+2k_3}\right\}$$

$RO_2NO_2 \xrightarrow{k_1}\xleftarrow{k_{-1}} RO_2 + NO_2$

$RO_2 + RO_2 \xrightarrow{k_3} 2RO + O_2$

$RO + NO_2 \xrightarrow{k_4} RONO_2$

Approach /Solution – Write decay differential equation

$$\frac{d}{dt}[RO_2NO_2] = -k_1[RO_2NO_2] - k_2[RO_2][NO_2]$$

and decay of RO_2

$$\frac{d}{dt}[RO_2] = k_1[RO_2NO_2] - k_2[RO_2][NO_2] - 2k_3[RO_2]$$

and, Of course!!

$$\frac{d}{dt}[RO_2] = 0$$

Once this derivative is 0, I think now it is very easy for you to find out what will be the k observed and that should relate to this concentration.

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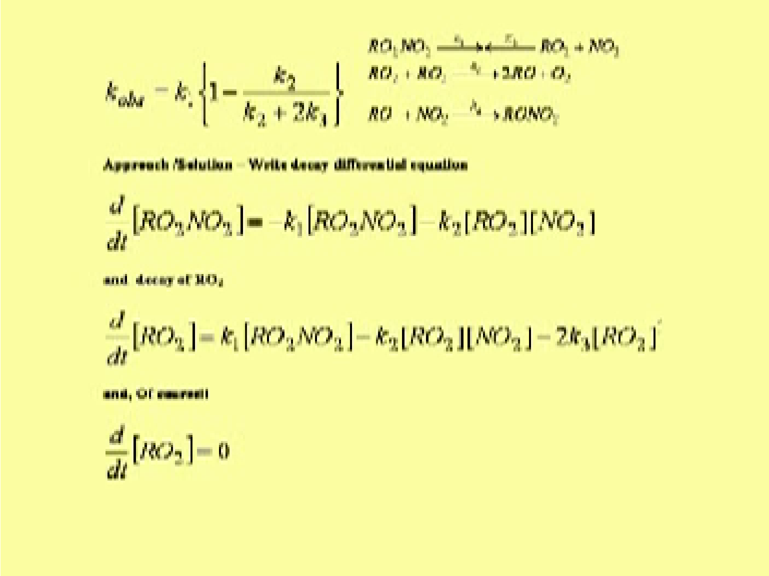

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and decay of RO_2

$$\frac{d}{dt}[RO_2] = k_1[RO_2NO_2] - k_2[RO_2][NO_2] - 2k_3[RO_2]$$

and, Of course!!

$$\frac{d}{dt}[RO_2] = 0$$

Try to do that. It is very simple and you will get that. Now, the question is…. In the question what we wanted to find out was… just see that. We wish to….

[Conversation between student and professor - Not Audible (17:09 min)]

For…?

[Conversation between student and professor - Not Audible (17:13 min)]

For RO_2NO_2, right? we wanted to find out k_1 and once you got this relationship how will you find k_1? [17:24] k_2 and k_3 are known. From the study that we have done in the box, what will we get? What will we get from here? Do not forget we are only measuring two things – time and the concentration of RO_2NO_2. What will I get from this kind of a graph? k observed. k observed. That is the k observed because you are observing the system, you are observing the system. This is not k_1 and that is what I am trying to tell you again and again, because there is a reaction after reaction, so this is k observed. You can put the k observed here and I am telling you k_2 and k_3 three are known, so you can find k_1.

That is how sometimes when the equations are interlinked, then you have to account for all those interlinked relationships. Your interest might sometimes be simply k observed but on purpose, I said you must estimate k_1 so that you can very clearly distinguish between what is k observed and what is k_1, which are two different things. If there is any question, let me know before we go to something else. We are back to our equation that we were discussing last time and we very carefully balanced that equation.

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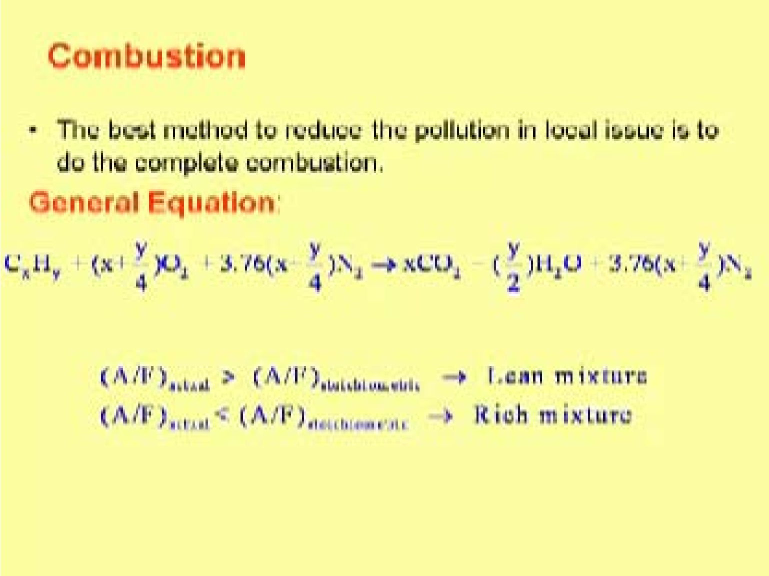

Combustion

- The best method to reduce the pollution in local issue is to do the complete combustion.

General Equation:

$$C_xH_y + (x+\frac{y}{4})O_2 + 3.76(x+\frac{y}{4})N_2 \rightarrow xCO_2 + (\frac{y}{2})H_2O + 3.76(x+\frac{y}{4})N_2$$

$(A/F)_{actual} > (A/F)_{stoichiometric}$ → Lean mixture

$(A/F)_{actual} < (A/F)_{stoichiometric}$ → Rich mixture

I also pointed out to you that it is a terrible mistake if you do not include nitrogen in the process. It is also a terrible mistake if you do not put proper moles of nitrogen – somebody can say that this can cancel with this. No, we do not cancel them because what we do is that we deal with the reactants differently – that is one thing you look at in isolation – and the products differently in isolation again. Then we also define that if air to fuel ratio, which is observed or actual, is more than this (Refer Slide Time: 19:38), then the mixture is a lean mixture for combustion and if it is less than stoichiometric, then we call this mixture as a rich mixture. That is all we had done.

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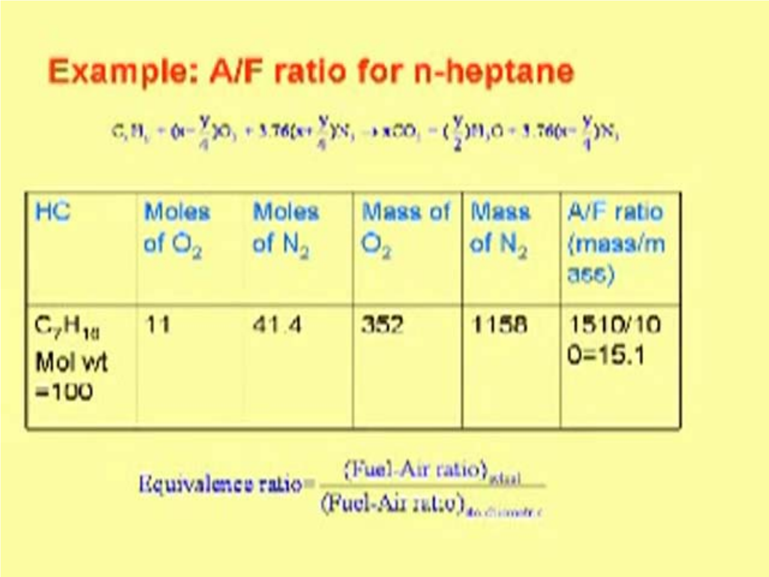

Example: A/F ratio for n-heptane

$$C_xH_y + (x+\frac{y}{4})O_2 + 3.76(x+\frac{y}{4})N_2 \rightarrow xCO_2 + (\frac{y}{2})H_2O + 3.76(x+\frac{y}{4})N_2$$

HC	Moles of O_2	Moles of N_2	Mass of O_2	Mass of N_2	A/F ratio (mass/mass)
C_7H_{16} Mol wt =100	11	41.4	352	1158	1510/100=15.1

$$\text{Equivalence ratio} = \frac{(\text{Fuel-Air ratio})_{actual}}{(\text{Fuel-Air ratio})_{stoichiometric}}$$

What I want to do now is do a very simple calculation, which you all can understand. You should make sure that you understand that. This is our basic fundamental equation. Suppose I am taking the example of an n-heptane, which is of the hydrocarbons used in the combustion process. n-heptane and octane are very common. Let us say this is the compound. Why I take this example is because calculations are easy – its molecular weight is very nicely placed at 100.

How many moles of this are there? 1 mole, correct? So how many moles of oxygen will be required? Is it 11? How? 7 plus 16 by 4. That makes it 11. Moles of nitrogen – 3.76 times of 11, correct? Can you get the moles? You can also get the mass of oxygen. 11 times 32, right? That is the mass. You can also get the mass of nitrogen. Now, can you find out the air to fuel ratio? What was the mass of the air that is entering in?

[Conversation between student and professor - Not Audible (21:23 min)]

Nitrogen plus oxygen. That makes it I am sure if you should add to 1510, if not, there is an error divided by the mass divided by the mass of the compound that you are burning. You got this equals to…. We have found out the air to fuel ratio at stoichiometry for n-heptane. Simple calculation – there is nothing big, simple thing. This is what is the equivalence ratio – (fuel to air ratio)$_{\text{actual}}$, then you can find out the equivalence ratio also. This is the stoichiometry.

For n-heptane, what is the (fuel to air ratio)$_{\text{stoichiometry}}$? 15.1. When you are doing here in the process, you find out your actual ratio. If the equivalence ratio is greater than 1, then is the mixture lean or is it rich? Lean. Okay, that is right. So you understand that. These are the simple calculations but very important calculations. Let us go down.

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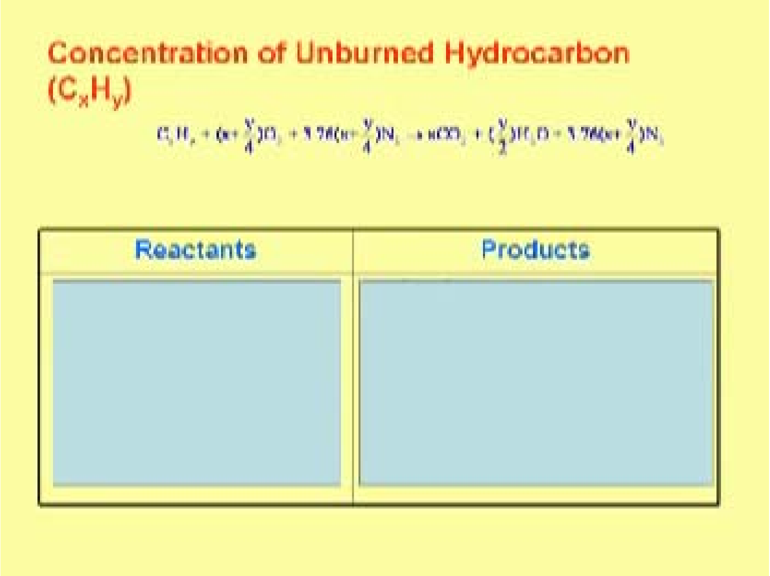

Concentration of Unburned Hydrocarbon (C_xH_y)

$$C_xH_y + (x+\frac{y}{4})O_2 + 3.76(x+\frac{y}{4})N_2 \rightarrow xCO_2 + (\frac{y}{2})H_2O + 3.76(x+\frac{y}{4})N_2$$

Reactants	Products

Now, I am writing this equation again because that is the fundamental equation and every time, you need to refer to this equation. Sometimes, air pollution engineers or air pollution scientists or combustion engineers will be greatly interested in things here – what is reacting with what, what quantity and so on. You go to a plant and you ask a person operating there what he is doing, he will simply say that he is maintaining the oxygen level. That is what his job is but if you ask an environmental engineer or air pollution engineer what he is observing, he would say he is observing the reactants that are going out in the ambient air. So there is a difference in what people observe.

Let us divide the whole thing between reactants and products and I am writing them in the molar form.

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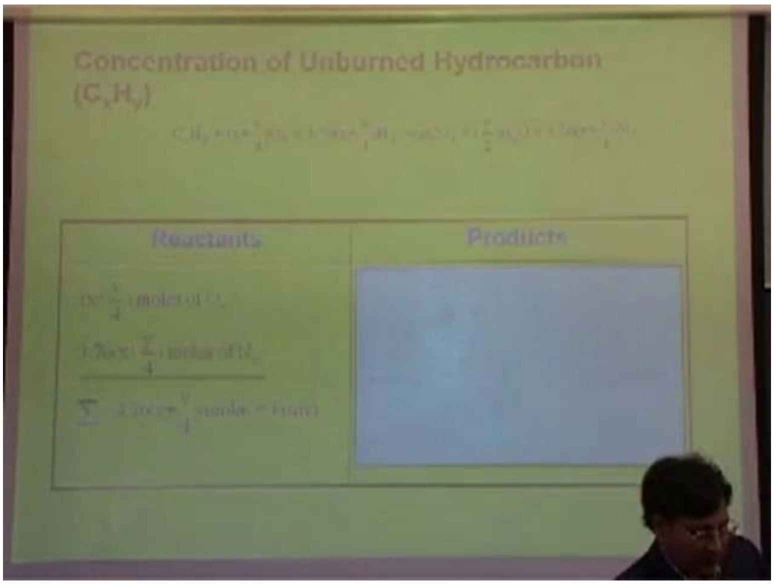

Concentration of Unburned Hydrocarbon (C_xH_y)

Reactants

Products

I can look at the total moles, there is no problem – we know how many moles of oxygen (Refer Slide Time: 23:50) and so many moles of nitrogen. We add them up and you find so many moles of reactants. Let us call that as F. Similarly, I can write the products.

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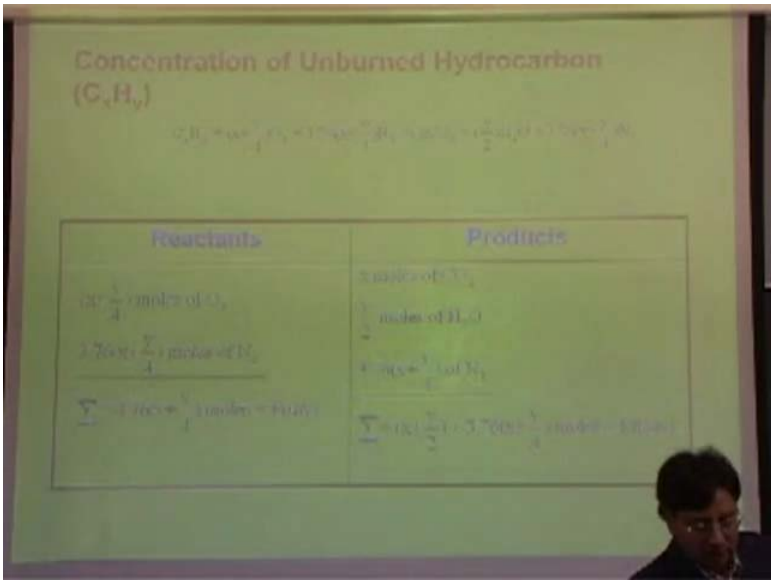

Concentration of Unburned Hydrocarbon (C_xH_y)

Reactants

Products

Simple job, nothing very difficult. You can write this and then M. Remember that we are having reactants as F in terms of mole and we are having the products also in the form of moles. We are calling that as M and this we are calling as F. Now, we will come to a little bit of air pollution. Maybe combustion engineers can still talk many things about this.

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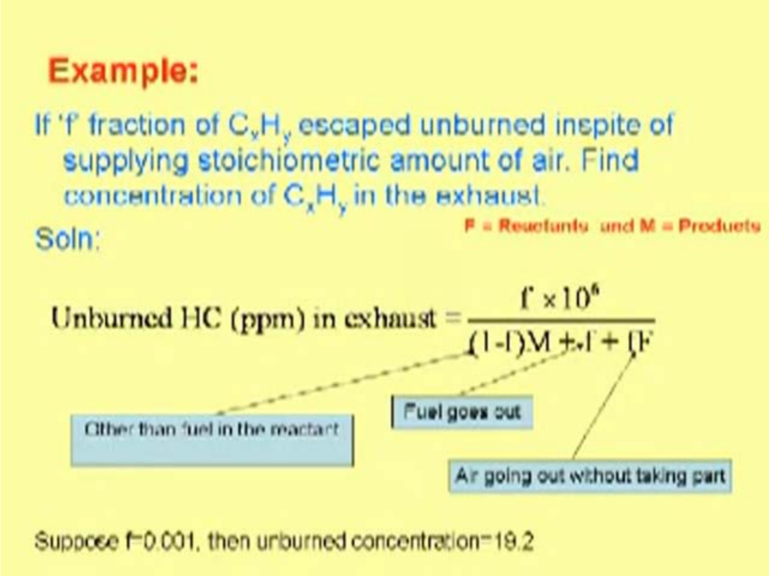

Example:

If 'f' fraction of C_xH_y escaped unburned inspite of supplying stoichiometric amount of air. Find concentration of C_xH_y in the exhaust.

Soln:

F = Reactants and M = Products

$$\text{Unburned HC (ppm) in exhaust} = \frac{f \times 10^6}{(1-f)M + xf + fF}$$

Other than fuel in the reactant

Fuel goes out

Air going out without taking part

Suppose f=0.001, then unburned concentration=19.2

Now I am going to give you an example of how the air pollution engineers want to utilize…. This is a little knowledge that we need for combustion engineering – not a great deal of knowledge that we need. It really happens and it is happening all the time. When I say fraction, I am talking about the molar fraction because we are talking of moles – nothing to get confused now. Suppose a fraction f of the hydrocarbon that you are burning escapes unburned, it did not participate. There could be many reasons – the temperature was not right, the [25:22] time for the reaction to happen was not timed, there was not enough turbulence in the system

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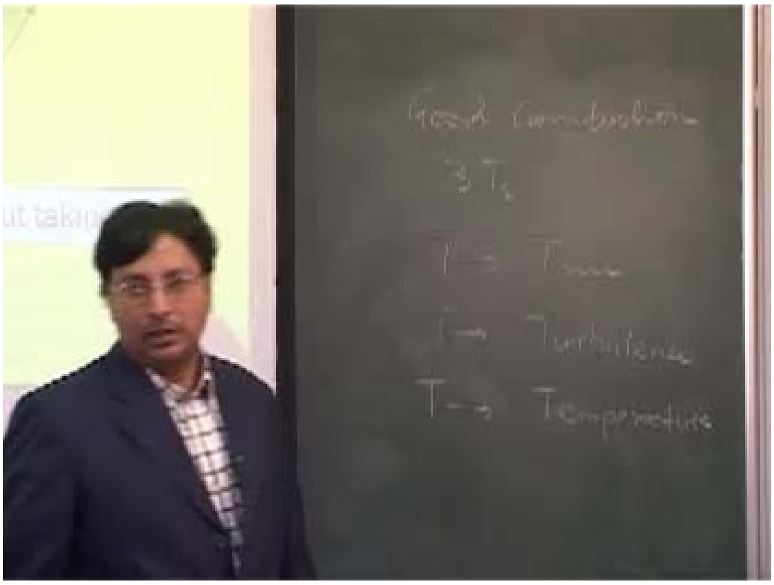

For the combustion engineering, good combustion, three Ts are important. You have to give enough time for the reaction to happen. You have to have the right amount of turbulence (there is an opportunity – combustion is a surface phenomenon); if there is no turbulence, you cannot have proper combustion. The third and very important is temperature. If you do not have these three Ts properly, things go unburned.

Suppose something went wrong and some fraction of the thing went unburned in spite of supplying stoichiometric… we supply stoichiometric amount of air, find the concentration of… Now, this becomes a pollutant for me (Refer Slide Time: 26:42) and so I am interested in what kind of concentration, what kind of emissions of the hydrocarbon will show up in my product. As an engineer of air pollution, I am interested in the product rather than in the reactants. That is what we are trying to do. Do not forget F was the reactants and M was the products.

Now unburned hydrocarbon in the exhaust and the units I am giving is ppm. The unburned is F mole into million thing parts per million to 10 to the power of 6. Now, you have to really figure out what all is there in the exhaust. 1 minus F time M. What was the M? It was for the products, but if this was 0, the product was M, this thing did not burn (Refer Slide Time: 27:46), so I did not need this. The product is 1 minus F times M. Simple thing. Plus F, the quantity of the unburned fuel that went out – this is very very small of course plus the air that did not react – we supplied air but it did not react.

How much of the air did not react will show up as such of the product as such all those reactants into the product. That is F times f. Let me tell you if f was 0, then the combustion will complete. This term becomes 0, correct? This is the term that denotes that air is going out without taking part as such. Otherwise, this would be taken care into the M. Yes?

[Conversation between student and professor - Not Audible (28:44 min)]

Everything is in moles.

[Conversation between student and professor - Not Audible (28:47 min)]

Yes.

[Conversation between student and professor - Not Audible (28:50 min)]

In what units is the fraction in? Fraction will be in…. It is a mole fraction, it is the mole fraction of the hydrocarbon that we are considering. How many moles of the hydrocarbon had we considered in our example? Please tell me that. The first thing when we are finding out the products and the reactants. 1 mole. C_xH_y was only 1 in front. There is one mole, so a fraction of that 1 mole escaped unburned. Does that answer your question? All right.

This is the situation. We are taking the same example. Suppose F is 0.001, I think this example is for n-heptane only, then the unburned (which is of interest to me as an air pollution engineer) could be about 90.2 ppm. Such a small amount went unburned, we are talking about n-heptane, so that is constant. You can do some calculation. Please check that so that you can understand this. Take another assignment.

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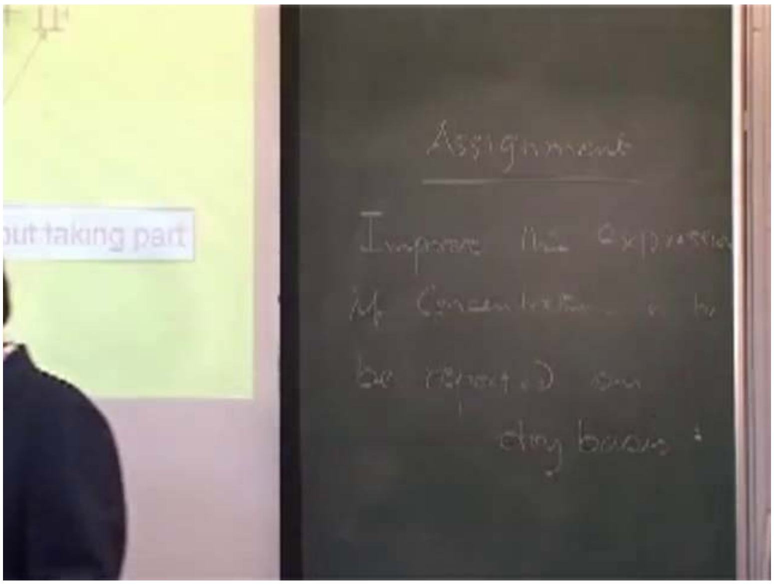

Assignment

Improve the expression of concentration to be reported on dry basis.

Improve or re-derive. Improve the expression if concentration is to be reported on dry basis. Many times, we want to express things on a dry basis. You should try this. This is not so difficult. What is to be done? Take the water component out from the products. Dry basis means you are not considering the water component.

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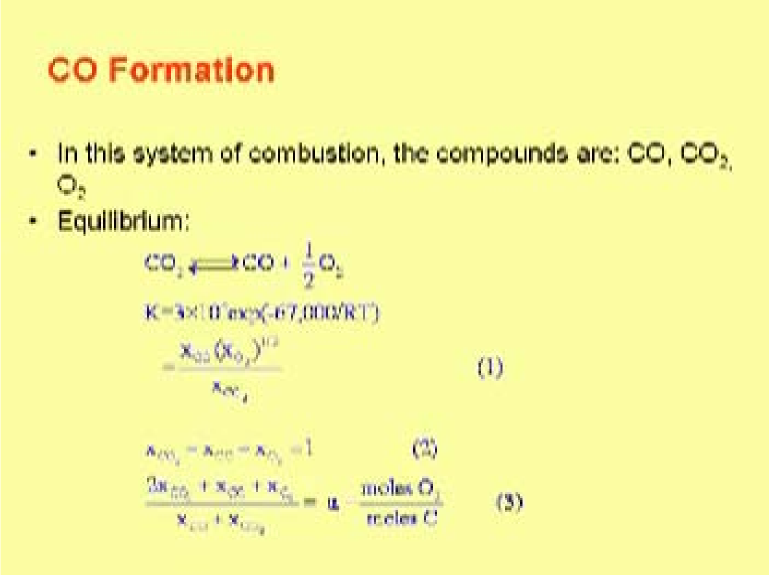

CO Formation

- In this system of combustion, the compounds are: CO, CO_2, O_2
- Equilibrium:

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$$

K = 3×10 [illegible] exp(-67,000/RT)

$$= \frac{x_{CO}(x_{O_2})^{1/2}}{x_{CO_2}} \qquad (1)$$

$$x_{CO_2} + x_{CO} + x_{O_2} = 1 \qquad (2)$$

$$\frac{2x_{CO_2} + x_{CO} + x_{O_2}}{x_{CO} + x_{CO_2}} = a = \frac{\text{moles O}}{\text{moles C}} \qquad (3)$$

We will get more into combustion now and look at the formation of carbon monoxide. Let us have a look. We all understand the reactions for carbon monoxide. It is essentially the formation of CO_2, which goes back and forth with carbon monoxide. This is the standard equation that you all understand very well. What are the components we are considering right now? There are three components – CO, CO_2 and oxygen. What happens is the value of k is given and I can write k equals to…. What I am trying to write here is…. I am assuming the total moles as 1 mole in the system.

There will be some mole fraction in terms of CO_2, some mole fraction in terms of CO and some mole fraction in terms of oxygen – 1 mole I am considering. Suppose I want to write the ratio from these equations, then let us write the ratio of the moles of oxygen to the moles of carbon. I am trying to write down the moles of oxygen. How many moles of O (you can say basically O), how many moles? If I am considering in CO_2, how many moles of O? 2 – because this is 2, this is 2 here. Then in terms of CO, how many moles of oxygen? 1. 1, so there is 1. Then oxygen – there has to be 2, there has to be 2 XO_2, there has to be 2. Then, moles of carbon. How many moles of carbon?

[Conversation between student and professor - Not Audible (33:28 min)]

Because oxygen is 2. You can say moles of O or the mass of O. If this is 2 (Refer Slide Time: 33:41), this also has to be 2.

[Conversation between student and professor - Not Audible (33:44 min)]

No, that is different. Now, I am not looking at the equation. I have a process in which I have the mole fraction of this, mole fraction of this and mole fraction of this. Forget about…. Suppose I even take the volume of the air here and look at this – take some fraction of CO_2. Out of that, how much will be O_2?

[Conversation between student and professor - Not Audible (34:09 min)]

Then for O? 2? You see 2 here. Then talking about the C, I have two species – the carbon here will give you 1 here and this carbon will give you 1.

[Conversation between student and professor - Not Audible (34:31 min)]

Why?

[Conversation between student and professor - Not Audible (34:35 min)]

No. How many moles of carbon are here? 1 because the subscript is 1 here and there is 1 here. What I will write will be 1 only but this is the correction that this should be 2, so 2. You have understood that. Now, I want to find out the concentration of CO in the process. How many are known and unknown? We have three unknown situations – CO_2, CO and O and we have three equations. I can certainly vary alpha and disturb the combustion process if I like. I can change alpha, I can put in more oxygen, I can put less oxygen and as a result, my alpha will change. Let us do that and see that how this thing and this thing…. (Refer Slide Time: 35:40).

The whole thing will depend on alpha and on k of course. What does k depend on? Temperature. k depends on temperature. As my temperature changes, so will my concentration. I do not know how that will change – we will figure it out. If I change my alpha, if I am putting more oxygen, things might be different. If I am putting more carbon, but…. What is that which is in my hand to operate? C or O? Oxygen. Oxygen generally. By and large, you are putting the same amount of fuel – that is fixed. Combustion engineers will vary the air amount. Generally, when we think about the alpha, we are really changing the oxygen.

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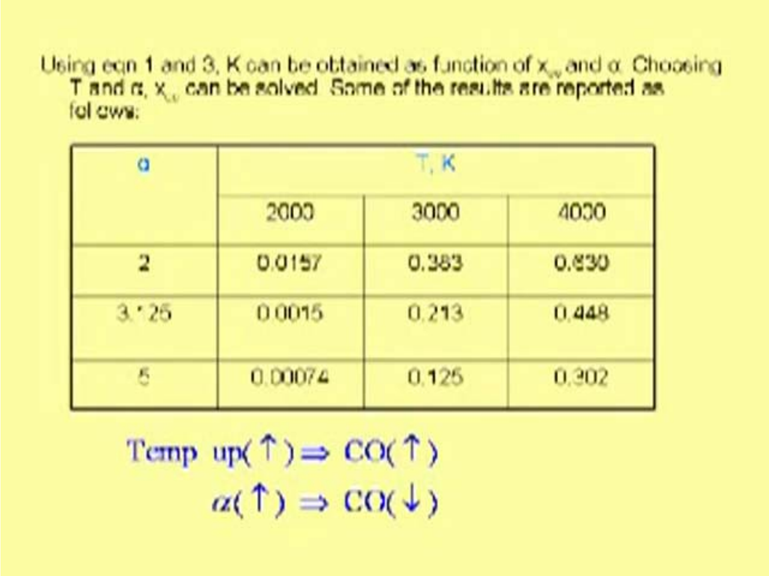

Using eqn 1 and 3, K can be obtained as function of x_{co} and α. Choosing T and α, x_{co} can be solved. Some of the results are reported as follows:

α	T, K		
	2000	3000	4000
2	0.0157	0.383	0.830
3.125	0.0015	0.213	0.448
5	0.00074	0.125	0.302

$$\text{Temp up}(\uparrow) \Rightarrow CO(\uparrow)$$
$$\alpha(\uparrow) \Rightarrow CO(\downarrow)$$

Look at the final thing. Here, I have the temperature – I am utilizing that knowledge and the alpha and what I am trying to look at is the mole fraction of CO. That is what I want to say – how CO formation will depend on temperature and alpha. What can you see? What was the alpha – O by C ratio? I am supplying more and more of oxygen. What should happen? Combustion should be complete. I am supplying more and more of oxygen and my CO quantity should decrease. It does decrease. That will be the case here and here.

But if from the same expression I am increasing the temperature of my combustion, if I am increasing the temperature of combustion, this is the fraction mole of CO and this mole went up (Refer Slide Time: 37:41). You can do this calculation yourself. I increase the temperature even more. Of course, the situation is the same [37:50] CO. This is the summary here. When the temperature is up, the CO is up and when alpha is up, CO is down. Alpha is up means I am putting in more oxygen.

Whatever little science we learn, we should again apply it to a process so that we can benefit from the science that we learned. Science is not just for writing on the board, science is not for getting good marks alone – science must be used. That is what we do all the time. Science must be used. If I want to manage CO I think I should make sure that the combustion temperature is low and I supply enough amount of oxygen as is seen here. Let us do the next example, let us look at the formation of NO_x.

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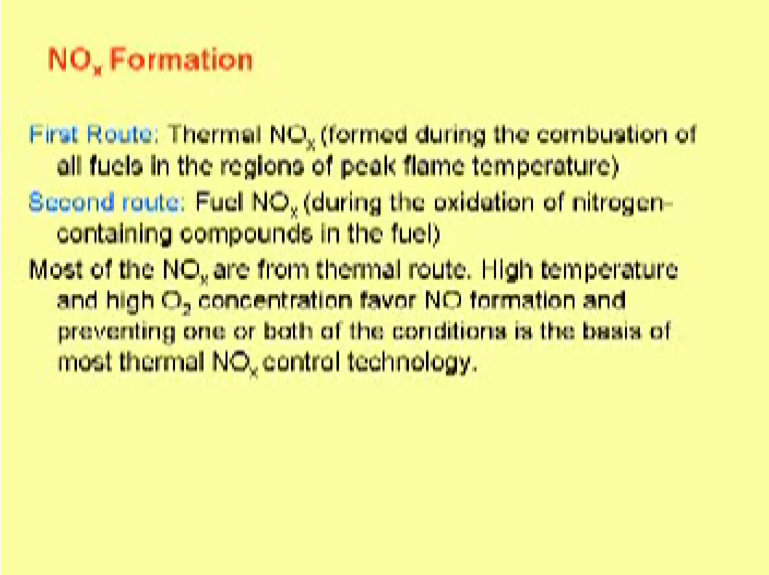

NO_x Formation

First Route: Thermal NO_x (formed during the combustion of all fuels in the regions of peak flame temperature)

Second route: Fuel NO_x (during the oxidation of nitrogen-containing compounds in the fuel)

Most of the NO_x are from thermal route. High temperature and high O_2 concentration favor NO formation and preventing one or both of the conditions is the basis of most thermal NO_x control technology.

NO_x is a very very interesting thing and it can form through two routes. There is one more route called instant NO_x, but that is very very small. We will not talk about instant NO_x but we should talk about the two routes. The first route is the thermal NO_x. Thermal NO_x is formed during the combustion processes as combustion of all fuels in the region of peak flame temperature. You are providing enough oxygen and enough temperature.

(Refer Slide Time: 39:40)

which we said do not react but that is not the correct case – they can react and can form the gas. It is certainly a possibility and a good amount of NO can be formed. Do you know any source of NO other than combustion? Volcanoes. Volcanoes. Other than that? Lightning. Lightning. It is not a very small amount, it is really not a small amount. The lightning that happens in the atmosphere…. We just see the lightening and sometimes enjoy or get scared but the temperatures there become huge. It is such a high temperature. Nitrogen and oxygen are there any way and so that reaction produces NO and also sometimes NO_2 – could be could be a significant amount. It happens in the higher altitudes and it can affect the chemistry at the higher altitude.

What we have said here is that this can happen in the combustion process in the presence of heat. This is the atmospheric nitrogen and this is of course atmospheric. That is one route. This is very much temperature dependent –we will show you that in a moment. It also depends on the temperature. The oxygen that you are putting or let me say the air that you are putting in the combustion process will cause the emission of NO, but there could be another route also. What is the other route? Fuel NO_x. It means the amount of nitrogen that was present in the fuel may get burned out as the oxides of nitrogen.

Fuel NO_x – during the oxidation of the nitrogen containing compounds in the fuel. What you need to see here is that most of the NO_x are from the thermal route generally, unless you are talking of a great deal of nitrogen or presence of nitrogen in the fuel itself. Most of the NO_x are from through the thermal route. High temperature and high oxygen content favor NO formation and preventing one or the other condition is the basis for most of the control of NO_x in the combustion process. What is important here? Two things.

If this reaction is happening, what is the rate-limiting species in the combustion process, which can limit the rate of formation – is it nitrogen or oxygen? Oxygen. Oxygen, because nitrogen is in plenty – 78 percent is nitrogen. Who cares whether nitrogen is decreasing or increasing? The rate-limiting species is oxygen. The other rate-limiting species is the heat. Whenever you are talking about control, talk about O_2 and temperature. You should try not to give too much of excess air and you should also try to see that the temperatures do not go very high if you want to really control the NO_x.

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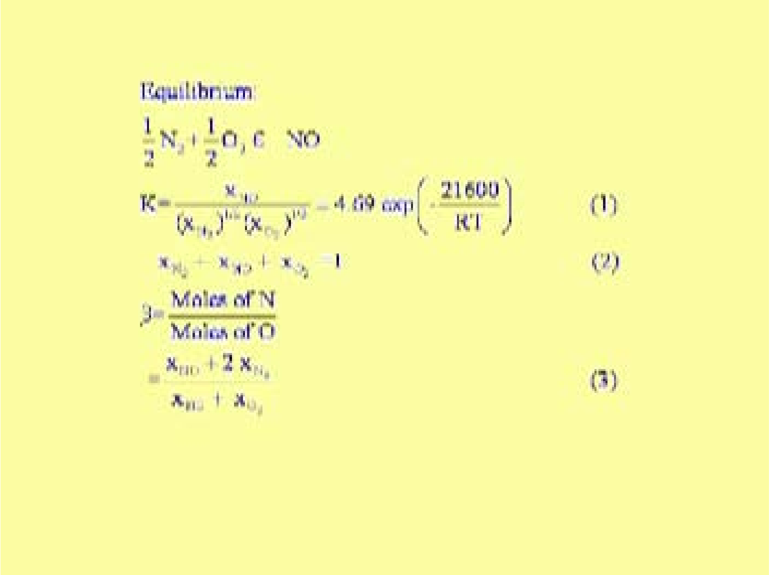

Equilibrium:

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \; C \quad NO$$

$$K = \frac{x_{NO}}{(x_{N_2})^{1/2}(x_{O_2})^{1/2}} = 4.69 \exp\left(-\frac{21600}{RT}\right) \qquad (1)$$

$$x_{N_2} + x_{NO} + x_{O_2} = 1 \qquad (2)$$

$$\beta = \frac{\text{Moles of N}}{\text{Moles of O}}$$

$$= \frac{x_{NO} + 2\,x_{N_2}}{x_{NO} + x_{O_2}} \qquad (3)$$

That is what we said here. Let us look at the same kind of relationship now with respect to what is happening with the NO. You see here equal to NO. Then, K is the equilibrium constant. You can see X and O, there is no problem in this relationship. I will send you the slides so that you can see. Same idea but this time, the situation is reversed. Last time, we looked at O by C, right? Here, I am looking at N by O. There is a reason – I will explain that to you.

Let us go back and see and try to have a look at what the student asked – the moles of nitrogen here. How many moles of nitrogen here? 1. 1. How many moles of nitrogen here? 2. 2. How many moles of oxygen here? 1. 1. This should be again 2. That is what you get. Again, I can produce a similar kind of table to show much NO will be produced and how it will depend on… which we are trying to answer depends on oxygen and temperature. Let us quickly look at the… Now, look at the relationship that we got. We have the beta here and beta was what? N by O. N by O.

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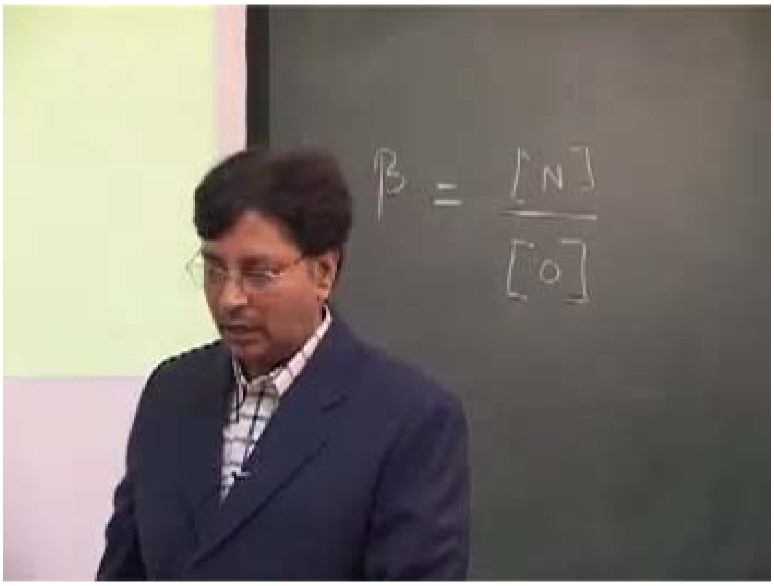

Then, what we are finding here is….

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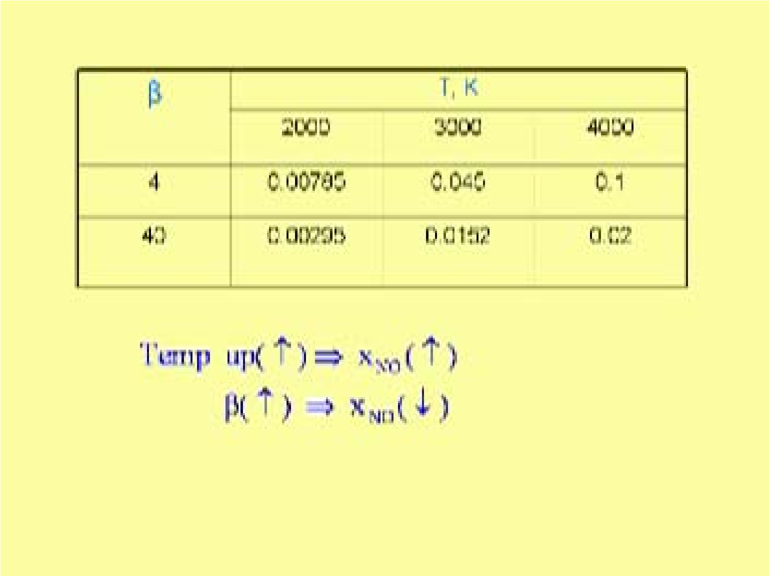

β	T, K		
	2000	3000	4000
4	0.00785	0.045	0.1
40	0.00295	0.0152	0.02

$$\text{Temp up}(\uparrow) \Rightarrow x_{NO}(\uparrow)$$

$$\beta(\uparrow) \Rightarrow x_{NO}(\downarrow)$$

As the temperature is increasing, the formation of NO_x or NO…. Clear? Now, let us have a look at the beta. Beta is 4. When I say the beta is 4, what it really means? I am…?

[Conversation between student and professor - Not Audible (46:08 min)]

That is correct but in my combustion process, where am I?

[Conversation between student and professor - Not Audible (46:13 min)]

Where am I in terms of air to fuel ratio? I am very very close to stoichiometry. What is the ratio of N by O in the atmosphere? 3.76. What is that? 4. So I am very very close to stoichiometry. The chances of forming NO is very little, but if I am giving a high temperature, the oxygen to be used in the combustion process or burning your hydrocarbon will also have the opportunity to react with the nitrogen because of the high temperature. Suppose I increase excessively the beta, if I am increasing excessively beta…. Am I increasing? Yes. What am I increasing really? [47:16] increasing or decreasing. This beta will increase because of increase in N or decrease in O? Decrease in O. Decrease in O.

When I am increasing this, when I am increasing beta, it means I am decreasing O so it means I am supplying…. Less oxygen. Less oxygen, so the opportunity for the formation of NO_x should reduce. Is it reducing? I am not sure, but let us see. It reduces from 7 to 2, it reduce from 4 or 0.4 to 1 and it reduces from 0.1. You see here, somebody can argue that beta can be manipulated with nitrogen or oxygen. The nitrogen is anyway there. It is the oxygen that we should really consider, because that oxygen is what is primarily responsible for combustion. The oxygen quantity that we supply depends on the combustion. If I look at beta being 40, it means this quantity (Refer Slide Time: 48:22) has to be less. Then you see the effect of the same thing we are talking about – the effect of oxygen and temperature. If you supply excess air, more is the NO formation. If you are operating your combustion process at a high temperature, then you are likely to produce more NO. Let us also make things a little bit more complicated and look at the formation of NO_2.

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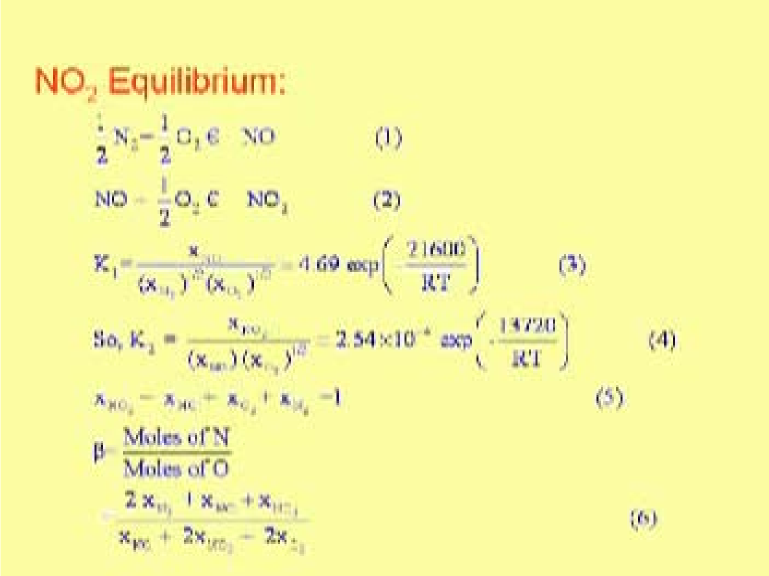

NO₂ Equilibrium:

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \Leftrightarrow NO \qquad (1)$$

$$NO + \frac{1}{2}O_2 \Leftrightarrow NO_2 \qquad (2)$$

$$K_1 = \frac{x_{NO}}{(x_{N_2})^{1/2}(x_{O_2})^{1/2}} = 4.69\exp\left(-\frac{21600}{RT}\right) \qquad (3)$$

$$\text{So, } K_2 = \frac{x_{NO_2}}{(x_{NO})(x_{O_2})^{1/2}} = 2.54\times10^{-4}\exp\left(-\frac{14720}{RT}\right) \qquad (4)$$

$$x_{NO_2} + x_{NO} + x_{O_2} + x_{N_2} = 1 \qquad (5)$$

$$\beta = \frac{\text{Moles of N}}{\text{Moles of O}} = \frac{2x_{N_2} + x_{NO} + x_{NO_2}}{x_{NO} + 2x_{NO_2} + 2x_{O_2}} \qquad (6)$$

The way the NO_2 is formed is again this is NO and generally, the NO gets oxidized to NO_2. Then, for these two equations, I can write k_1 and I can write k_2 – that expression is available to me and you know how to write that. Always keep it at the back of your mind that both k_1 and k_2 depend only on the temperature of the combustion. We see that clearly here. Now, I had not three species but four species – NO_2, NO, O_2 and N_2. The mole fraction of this, this, this plus this will be equal to 1, because I am taking them as the mole fractions.

I can redefine my beta again in terms of moles of nitrogen to moles of oxygen. Same thing that is here. Now, let us see. I have to consider all the species of the nitrogen-containing species – 2, 1 and 1. Now, look at the oxygen – 1, 2 and 2. This is more or less error free. I can take the beta – that is the variable. Now, what do you do here? What is my objective? It is to look at the formation of NO_2. How many unknowns are there? Four – one, two, three, four. How many equations am I getting? 1,2,3 and 4. Here, I am varying the beta. I can vary the beta and this expression that I will get for NO_2 is a little complicated but you can certainly try with computers. What will NO_2 be a function of? It will be largely a function of beta and temperature. Let us have a look at the situation as to what the picture looks like.

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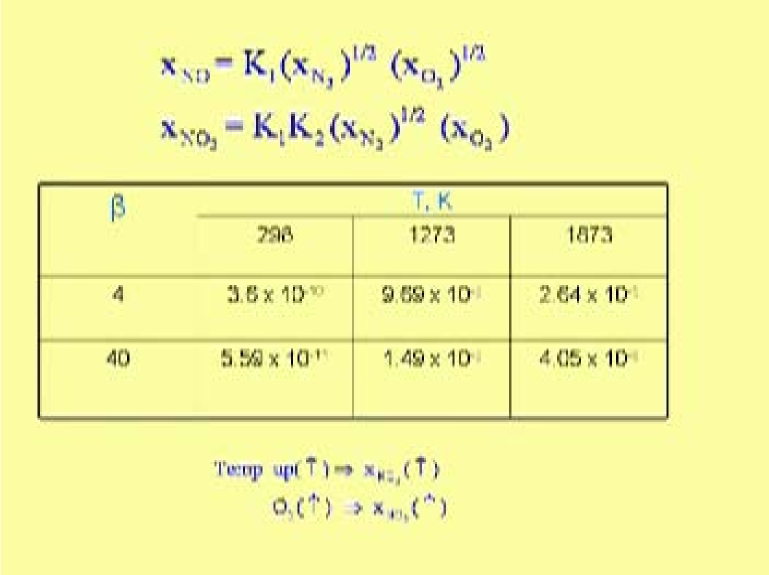

$$x_{NO} = K_1 (x_{N_2})^{1/2} (x_{O_2})^{1/2}$$

$$x_{NO_2} = K_1 K_2 (x_{N_2})^{1/2} (x_{O_2})$$

β	T, K		
	298	1273	1873
4	3.6×10^{-10}	9.69 x 10[illegible]	2.64 x 10[illegible]
40	5.58×10^{-11}	1.49 x 10[illegible]	4.05 x 10[illegible]

Temp up(↑) ⇒ x_{NO_2}(↑)

O_2(↑) ⇒ x_{NO_2}(↑)

That is from the equations. Once you solve this, I am taking the same beta – 4 and 40 and the same kind of temperature as this (Refer Slide Time: 51:40). Certainly, as the temperature increases, more and more of NO_2 will be formed. It is clearly seen. Simple – more of the NO will be formed, so there is more likelihood of NO to be formed. You have excess air, correct? Then what happens? I am sorry. When I have the deficit in the air. I am reducing O, I am sorry. When I am reducing O and there is less oxygen, it means formation should reduce from —10 to —11, —9 to 1 and then from —5 to –6.

If you compare this table of formation of the mole fraction of NO_2 vis-à-vis the table that I gave you for NO, what do you see? Let me complete the question – in terms of the quantities of NO and NO_2. You recall what were the NO quantities formed in the mole fraction if you have written them? It was something like 0.007, right? I can show you that. 0.007 or 0.045 (Refer Slide Time: 53:00). When I am looking at NO_2, it is one-millionth of that – 10 to the power of —10 or —11. We conclude that there is no possibility or a very little possibility of NO_2 being formed in the combustion process. You recall that I had explained you that what happens is…. I did not give the reason that time but if you recall, I did draw this picture and we will do it again quickly.

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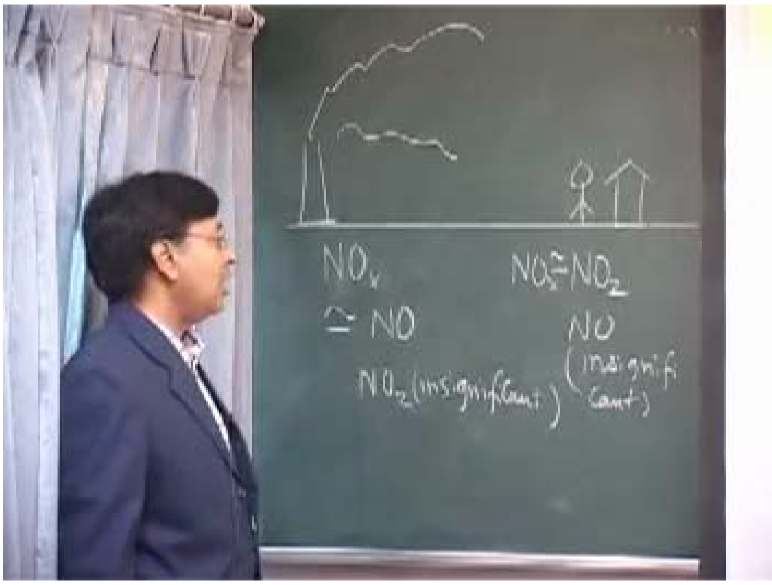

Almost if you like. There is no possibility of formation of NO_2 – we proved that. Last time, I just gave you this but now, you can very well be sure about this because NO_2 is insignificant. But by the time things travel, the picture changes and then, I have a good amount of NO_2. We have seen how NO_2 comes in the atmosphere, how it is formed in the atmosphere. It is because of ozone and because of hydrocarbons and other things. There are many factors in the atmosphere to oxidize NO into NO_2, which our combustion process could not do. The NO_x can nearly be equal to NO_2 because NO is somewhat insignificant.

Do not tell me that you are standing on the roadside at the GT road and you say "Sir, we you did this measurement and you were wrong. [55:23] largely NO"…. You are very close to the vehicle and if you are measuring at the GT road, then you will find this situation [55:33]. Receptor houses are there but if you are very very close to GT road, you will find mostly NO – you will not find NO_2. In a way, with the help of the combustion theory, we could explain as to how and under what condition what will be formed, what will be more, what will be less and so on. We also verified the little thing that I had given in the second, third or fourth lecture. I think we need to stop here. What is the time now? 12. 12? Very good. That worked out very well. We might talk a little bit more about NO_x in the next class – how to control and so on.