Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 13
Tutorial - 2

In tutorial 1, we have seen very basic problems related to the steam methane reforming and other hydrogen production methods. So, these were very preliminary knowledge about what type of problems can be associated with the course. Now, with that background let us see in this 2nd tutorial some more problems, these are more detailed problems.

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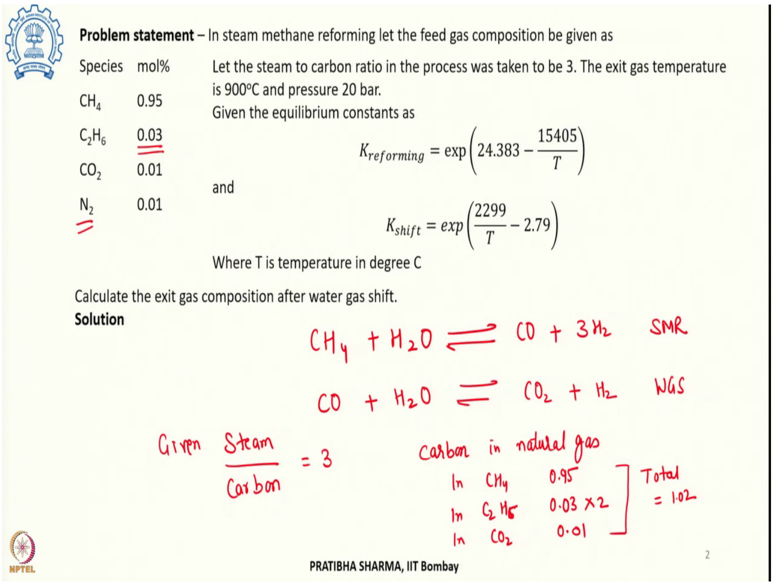

Let us look at the problem. The problem statement is that in a steam methane reforming reaction, the feed gas composition is provided. So, these are the different species which are present in the natural gas. So, in the earlier problem we have considered only methane being present.

Now, we know that natural gas is a mixed composition with methane primarily as major constituent, but then there can be other constituents as well. So, here we have taken other constituent to be ethane, carbon dioxide, nitrogen and let us assume that the steam to carbon ratio which is given in the process is 3.

So, steam to carbon ratio is provided to be 3 and the exit gas temperature is 900 degree centigrade and pressure is 20 bar, different equilibrium constants are provided, temperature T here is represented in degree centigrade. And, what we have to do is we have to calculate the exit gas composition after the two reactions, first steam methane reforming and then water gas shift reaction. Now, let us do this problem.

So, the first reaction that will occur is SMR and the second reaction will be water gas shift. It is given in the problem that steam to carbon ratio is 3. So, using that if we now calculate the carbon in the natural gas; so, we have methane in which the carbon is 0.95, mole percent of ethane is given which is 0.03 into 2, C 2 H 6 and also into the carbon dioxide which is 0.01. So, a total this all makes up a total of 1.02 moles.

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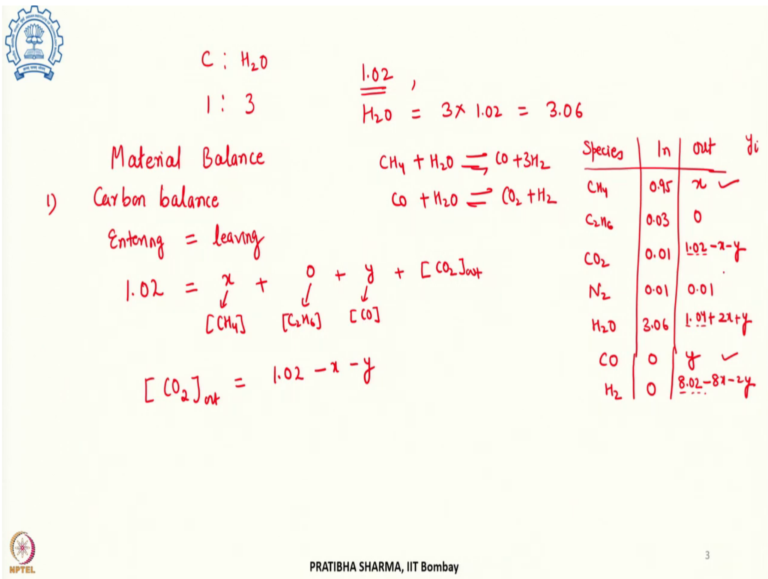

Now, if carbon to steam ratio which is given to be 1 is to 3 provided that its 1.02 mole percent of carbon. So, the steam is 3 times of this, which makes it to be 3.06 mole percent for steam. Now, there are two assumptions here. Nitrogen we know it remains unreacted in the process and we will assume here that the ethane is completely reacted in the reaction. So, to solve this problem, let us first write the species that is present at the inlet and at the outlet.

So, methane which is given to be 0.95, let us assume that in the outlet stream the unreacted methane is x, ethane C_2H_6 which is 0.03 mole percent. We assume that it is completely reacted, CO_2 0.01 that we will find out, N_2 given is 0.01. It is not consumed in the reaction, water we have just now seen it is 3.06. What comes out at the exit that we will find out. CO initially the initial mole percent was 0, let us assume that on reaction it is y, for H_2 initially it was 0 and then we will find out how much is there.

So, these are the entries that we need to fill in the table. Now, we will solve this problem using materials balance. Those who are from chemical engineering background they will be well versed with solving such problems, but we will be solving this simple problem, but a little lengthier one. So, we will be doing material balance and specifically atomic balance for each of these constituents. Now, if we do the material balance, we start with the carbon balance.

What we say is whatever is entering or being generated is equal to whatever is leaving, coming out. Now, if we start with the carbon balance, the carbon present at the inlet side is 1.02 that we have found and if we see the two reactions again here. So, now, what is leaving is unreacted methane. So, this is what is arising from the methane side x, then ethane it is completely consumed so, 0 for ethane.

Now, we have CO which is represented by y, the term arising from CO and then the term arising from CO_2. Let the CO_2 output, we will find from this carbon balance. So, the CO_2 at the outlet can be represented as 1.02 minus x minus y. So, this is one of the entry that we can fill here 1.02 minus x minus y. Now, the second material balance we will do will be for oxygen, if we do for oxygen balance again the same whatever is entering or generation equal to coming out.

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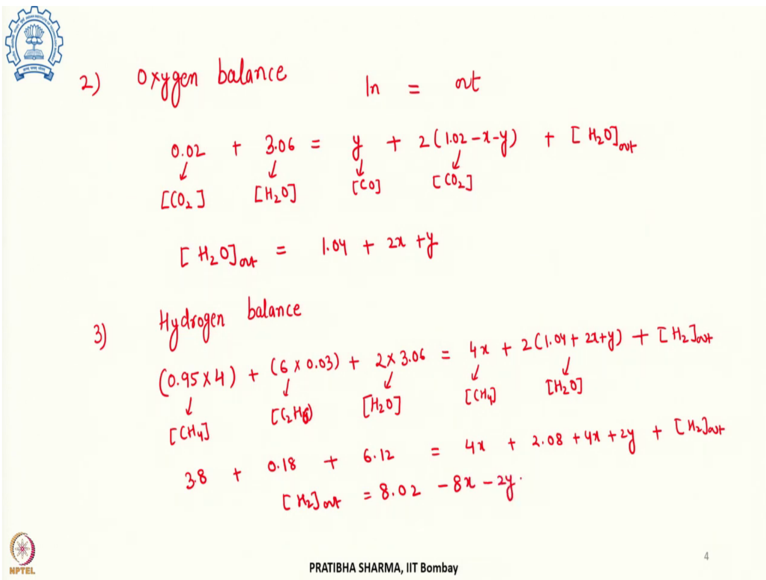

Now, from the CO_2 side it is 0.02 in the reaction which is entering with water so, it is 3.06, on the product side associated with CO its y. This is an atomic balance that we are doing, it is also associated with CO_2 we have just now calculated as 1.02 minus x minus y. So, we will substitute for that and there are 2 moles.

So, 1.02 minus x minus y that is arising from the CO_2 reactant and what in water also that oxygen content is there. Now, if with this oxygen balance we can find out the H_2O which is coming out and that comes out to be 1.04 plus 2 x plus y. So, in this table we have got the second entry which is that H_2O coming out 1.04 plus 2 x plus y. Now, the 3rd material balance we will do for hydrogen.

So, from methane, hydrogen is 0.95 in the reactant side and there are 4 hydrogen atoms to it. So, 0.95 into 4, this is arising from the methane in the reactant then there is ethane present on the reactant side. So, from ethane the mole fraction of it is 0.03 and then in ethane there are 6 atoms. Then it is coming from water, 2 water molecules reacting 3.06, 2 hydrogen atoms which are coming from water and the amount which is leaving that is corresponding to the unreacted methane, x amount of unreacted methane.

There are 4 hydrogen atoms in the methane. So, 4 x plus there is water 2 times 1.04 plus 2 x plus y. This hydrogen is having 2 atoms and hydrogen we have already found the content of it 1.04 plus 2 x plus y and that is along with the hydrogen coming out in the reaction. Now, if we solve this then we can write it as and that will give us the amount of hydrogen coming out and this corresponds to 8.02 minus 8 x minus 2 y.

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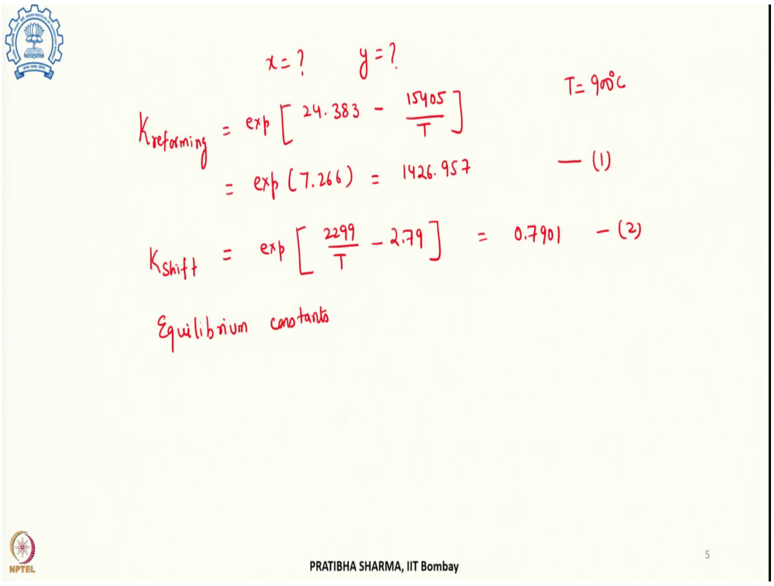

So, we will fill in this entry for hydrogen 8.02 minus 8 x minus 2 y. So, now, we have found the corresponding mole fraction of the species which are coming out in the process. Now, our aim is here to find out what are the values of x and y. To find this we have 2 unknowns and now we will be using the 2 known equations for finding these values of x and y. It is given in the problem that the equilibrium CO constant for the reforming reaction is given by exponential 24.383 minus 15405 divided by the temperature.

And, the temperature is also given in the problem to be 900 degree centigrade. So, we can find the reforming equilibrium constant and when we substitute this T equal to 900 degree centigrade, we get a value of. So, this exponential is exponential of 7.26 and that comes out to be 1426.957. So, this is one value we have got and similarly we can get the equilibrium coefficient for shift reaction.

It is provided from the correlation the value for shift is exponential 2299 divided by temperature minus 2.79. When we substitute again temperature equal to 900 degree, we get that value as 0.7901. So, now, we have 2 unknowns and we have 2 equations that we will be using. How we will frame those equations? We will be framing those equations according to the definition of equilibrium constant. So, equilibrium constants these 2 equations, these values we will be substituting in the definition for the equilibrium constants and then we will be getting. So, let us do one by one.

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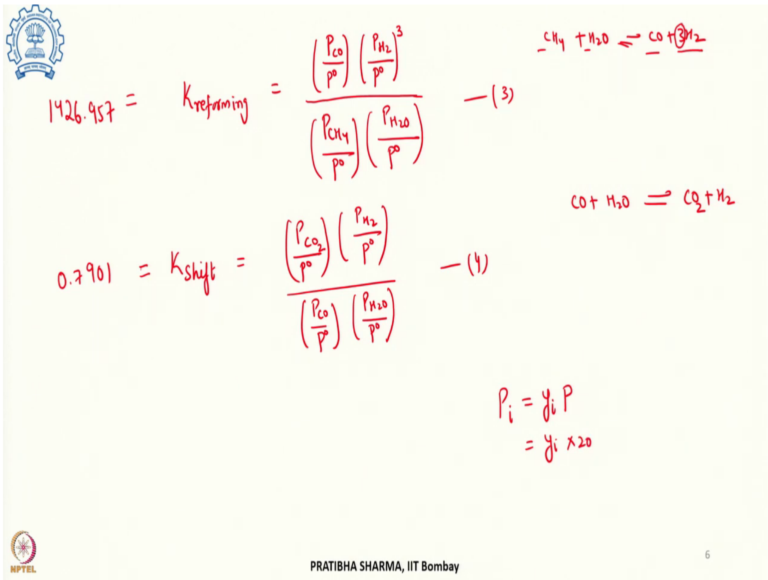

Let us first use for the reforming reaction the equilibrium constant. So, it is the partial pressure corresponding to the product side CO upon the standard pressure into the partial pressure for hydrogen which is one of the product upon the standard pressure raised to the stoichiometric coefficient. So, the reaction was CH_4 plus H_2O giving CO plus 3 H_2.

So, the product is CO, its partial pressure, partial pressure of hydrogen and the stoichiometric coefficient raised to the stoichiometric coefficient divided by the reactant side. So, the partial pressure of methane over the standard pressure, partial pressure of water divided by the standard pressure raise to the stoichiometric coefficient 1 and similarly we can do this for the shift reaction. So, shift reaction CO plus H_2O giving CO plus H_2.

So, the partial pressure of the product side CO over standard pressure, partial pressure for hydrogen. Similarly, for the reactant side CO_2, this is CO_2 and for hydrogen. Now, these are 2 equations whose values we have already found. So, for this particular problem the reforming equilibrium constant we have found to be 1426.957 and for shift reaction we have found this value to be 0.7901. Now, we will be substituting for the partial pressure in these equations to solve this problem.

Now, let us find out the partial pressures from the table which we have now filled the entries. So, we have the species known here and now we will be utilizing the Daltons law for finding the partial pressure. So, this is the species which we have got and now we can find the mole fraction from here. So, mole fraction we can calculate for each of these species, let us tabulate that separately. So, that we can use these for the finding the x and y values.

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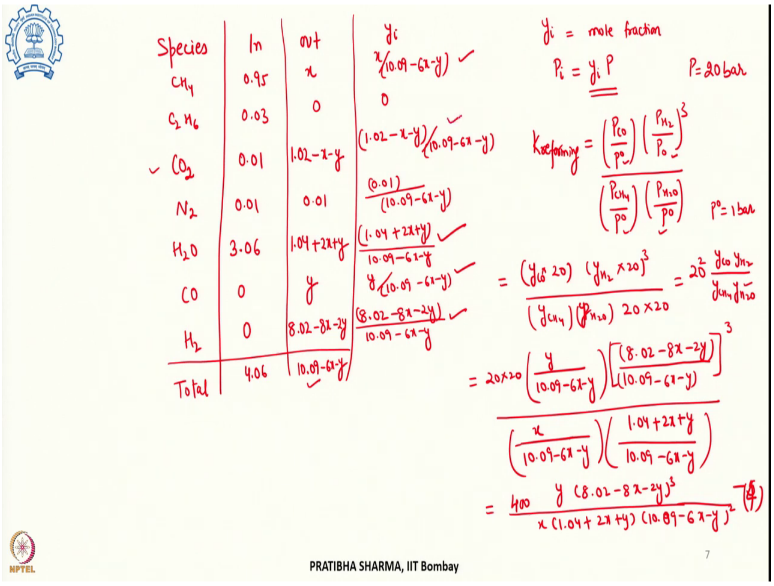

So, now if we try to evalute these again using the mole fractions then we can say that the species entering, leaving and corresponding mole fraction we can find. So, the methane on the reactant side 0.95, on the product side x, ethane 0.03 mole percent completely reacted, carbon dioxide 0.01. This was given in the problem and we have found that its content is in the outlet side is 1.02 minus x minus y. For nitrogen this remains unreacted, it was 0.01, it remains 0.01.

For water we have found it is 3.06 and then at the outlet side it is 1.04 plus 2 x plus y, for CO carbon monoxide initially it was 0. We have assumed its mole percent to be y on the product side, H_2 initially 0 and we have found it to be 8.02 minus 8 x minus 2 y. And, that total contributes to 4.06 entering moles, mole percent and then it leaving as10.09 minus 6 x minus y.

Now, we can find out the mole fraction corresponding to each of these species by dividing what we have got at the output divided by the total number of moles. So, for methane it is x divided by 10.09 minus 6 x minus y, for ethane this remains 0. For carbon dioxide it is 1.02 minus x minus y numerator, denominator is the total 10.09 minus 6 x minus y. For nitrogen again 10.09 minus 6 x minus y 1.04 plus 2 x plus y is the numerator, for water divided by 10.09 minus 6 x minus y, same for carbon monoxide; y divided by 10.09 minus 6 x minus y.

And, for hydrogen 8.02 minus 8 x minus 2 y divided by 10.09 minus 6 x minus y. So, this is the mole fraction, yi is mole fraction. Now, we know the relationship, partial pressure is equal to mole fraction times the total pressure and total pressure is given in the problem to be 20 bar. Now, substituting these individual mole fractions in the equilibrium constant in terms of the partial pressure. So, partial pressure will be given for any species i which could be CO, CH 4 or CO 2 or water.

We can write the partial pressure in terms of the mole fraction for that species and the total pressure which is 20 bar. So, yi into 20 and that we will substitute in the table here. Now, if we substitute for K reforming, the equilibrium constant for the reforming where we have just now seen it is the ratio of the partial pressure for CO, for hydrogen raise to the power 3. Similarly, for methane reactant side, the two reactants and steam.

Now, the standard pressure is taken as 1 bar, if we substitute all these values from terms of the mole fraction which is nothing, but yi times the total pressure, the denominator for each of these is 1. So, partial pressure for CO is given by the mole fraction for CO times the total pressure that is 20. Similarly, the mole fraction for hydrogen into 20 raise to the power 3, mole fraction for methane and mole fraction for hydrogen remains 20 to the power 2 and then the corresponding mole fractions for CO, hydrogen, methane and water; let us substitute those values. So, mole fraction for CO, we can use from here y divided by 10.09 minus 6 x minus y for the CO, for hydrogen 8.02 minus 8 x minus 2 y divided by 10.09 minus 6 x minus y whole raise to the power 3 stoichiometric coefficient. Denominator for methane x divided by 10.09 minus 6 x minus y.

And, the last term for water, this is given by 1.04 plus 2 x plus y divide by 10.09 minus 6 x minus 5. Now, this we need to solve, this is 1 equation that we will be getting. We can further simplify it to write this is whole cube divide by the denominator x 1.04 plus 2 x plus y and 10.09 minus 6 x minus y whole square. So, this is another equation which we have, let us write it as equation number 4.

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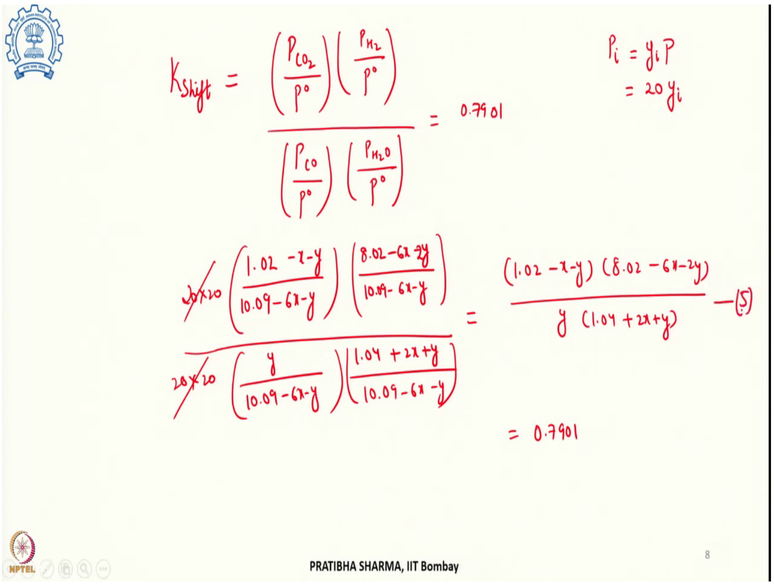

Same way we will be using for the shift reaction, the equilibrium constant for the shift reaction. There we have written the partial pressure for CO_2 for hydrogen divide by the reactants, partial pressure for CO and water. And, this value we have already calculated to be 0.7901. Now, let us again substitute the value for the mole fraction. So, partial pressure for species i is nothing but mole fraction times the total pressure and that is the 20 bar which is the total pressure times the individual mole fraction.

Now, again we will use all these mole fraction from the table. So, for CO_2 the mole fraction is given by this, let us substitute that. So, for the $_{CO2}$ the mole fraction was 1.02 minus x minus y divided by 10.09 minus 6 x minus y, for hydrogen it is 8.02 minus 8 x minus 2 y divided by the same denominator, we will substitute that 8.02 minus 6 x minus y divided by 10. 2 y 10.09 minus 6 x minus y. Similarly, for CO this is y divided by the same denominator 10.09 minus 6 x minus y and for water that is 1.04 plus 2 x plus y and, the denominator is same.

We also have total pressure for both the terms which gets cancelled out and that gives us 1.02 minus x minus y 8.02 minus 6 x minus 2 y divide by y 1.04 plus 2 x plus y and that is equal to 0.7901. So, these are the 2 equations, the equation number 4 and equation number 5, that we need to solve simultaneously.

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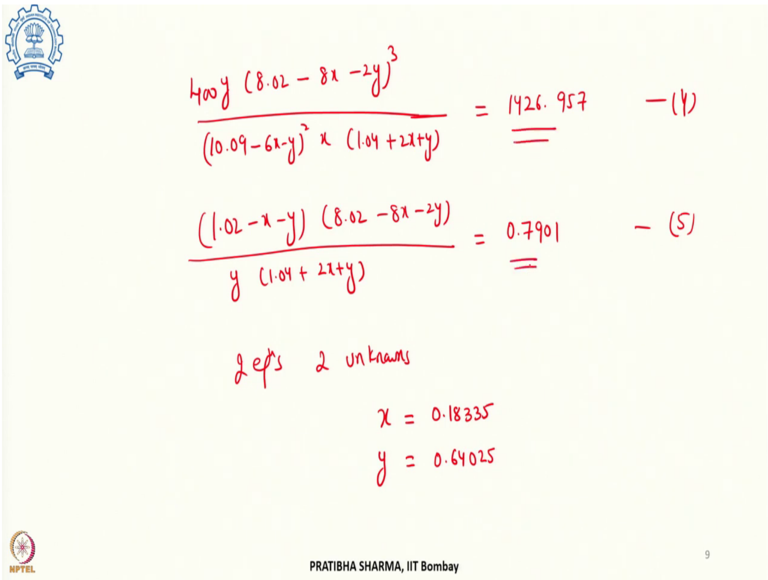

The 2 equations that we need to solve is y 8.02 minus 8 x minus 2 y whole cube 400 10.09 minus 6 x minus y whole square x 1.04 plus 2 x plus y. And, that value was equal to the reforming constant that was 1426.957. This is the equation number 4 rewritten here; 1.02 minus x minus y 8.02 minus 8 x minus 2 y divided by y times 1.04 plus 2 x plus y and that value is equal to 0.7901.

So, that is again the equation number 5 being rewritten. Now, we can see that these are polynomial equations that with fractions and that needs to be solved to find for the x and y. So, we have 2 equations and 2 unknowns. So, we need to solve that, it is little difficult to solve it. We can use Excel to solve and find out, we can use solver to solve and find out. And, if we solve that we can find out that the value of x comes out to be 0.18335 and, the value of y comes out to be 0.64025.

So, these can be easily solved by putting a value for x and y and then later on changing that value of x and y; so, that we can get very closer to these solutions.

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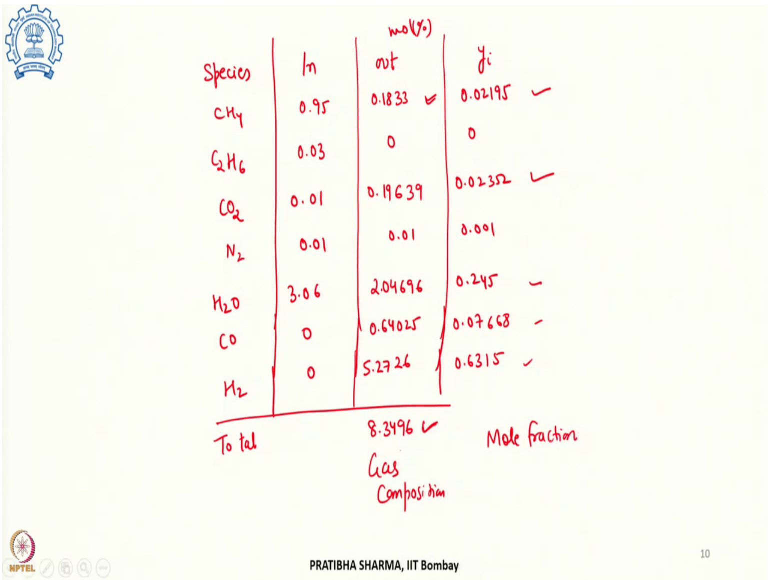

Now, if we put these values of x and y which we have just now found using these equations; in that case we can write down for the different species, the amount entering, amount leaving and the mole fraction for the various constituents in the reaction. For methane let us say it is 0.95, that was given; if we substitute the value of x, it is 0.1833. And, then we can find the later the mole fraction, for ethane that initially was 0.03 mole percent and that completely reacted. So, the at the output the mole fraction was 0, CO_2 it was given to be 0.01.

And, substituting the values we have found it is 0.19; 0.19639, for nitrogen this remain unreacted to 0.01, for water 3.06 we have found. And, then substituting the different values we get 2.04696, the values of x and y in the earlier table. For CO initially it was 0, hydrogen it was initially 0.

Now, substituting x and y we can get it to be 0.64025, for hydrogen 5.272. And, then if we do a total of it then at the exit this comes out to be 8.3496. So, mole percent divided by the total number of moles will give us the mole fraction. So, if we divide 0.1833 for methane with the total number of moles, we get it to be 0.02195. This is the mole fraction of the unreacted methane in the outlet gas stream.

Same for carbon dioxide, it is 0.02352, that is the carbon dioxide left after the reaction for nitrogen, for water 0.245, for CO 0.07668 and hydrogen 0.6315. So, this is the mole fraction or this is the mole percent in the product gas, this is the gas composition which was required in the problem. And, this is the corresponding mole fraction of each of the constituent present in the outlet gas stream. So, this is one of the problem, a little detailed one that we have solved today.

Thank you.