Material and Energy Balance Computations
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Lecture –30
Single Phase Problems and Concept of Multi-Phase System

Hello everyone, Welcome back once again in NPTEL online certification course on material and energy balance computation. We were in the single and the multiphase system concepts and on that we started the understanding on the single phase problems.

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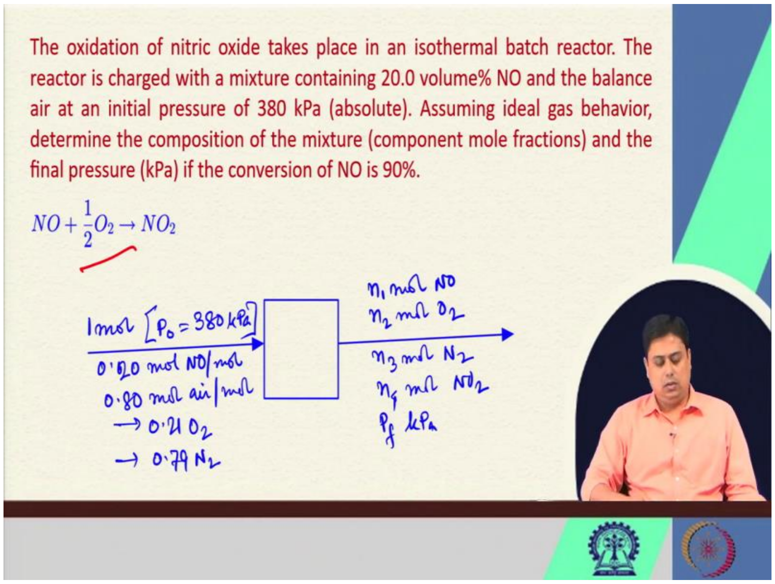

The oxidation of nitric oxide takes place in an isothermal batch reactor. The reactor is charged with a mixture containing 20.0 volume% NO and the balance air at an initial pressure of 380 kPa (absolute). Assuming ideal gas behavior, determine the composition of the mixture (component mole fractions) and the final pressure (kPa) if the conversion of NO is 90%.

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

And we tried to solve this problem in the last class and I wanted you to solve this problem before I show the solution and we stopped here that we identified we understood the problem and we identified that what is to be calculated. And what are the things that are unknown and what is the way we should solve the problem. On that methodology I told you that now we have a reaction involved and there is only a single reaction.

Now so, how do we solve this problem if we now go to the solution part. So, we have realized all these numbers by now.

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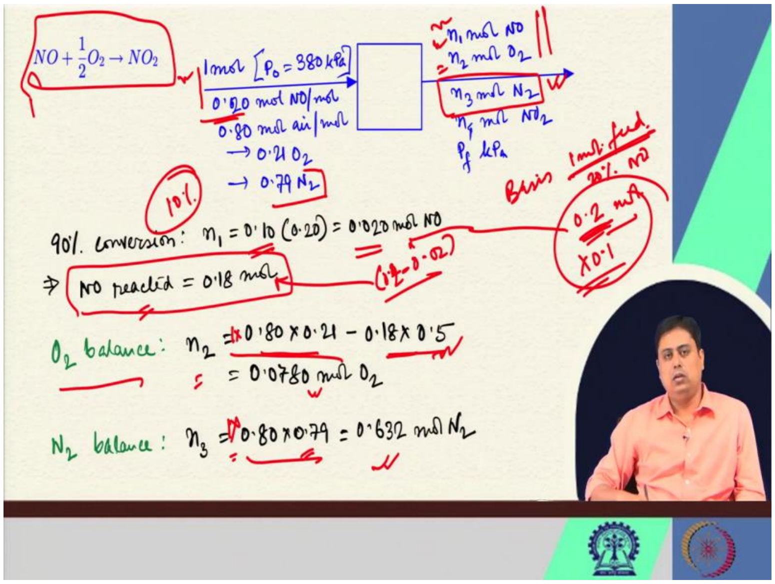

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

1 mol [P_0 = 380 kPa]

0.20 mol NO/mol

0.80 mol air/mol

→ 0.21 O_2

→ 0.79 N_2

n_1 mol NO

n_2 mol O_2

n_3 mol N_2

n_4 mol NO_2

P_f kPa

Basis 1 mol feed. 20% NO

0.2 mol ×0.1

10%

90% conversion: $n_1 = 0.10\,(0.20) = 0.020$ mol NO

⇒ NO reacted = 0.18 mol ← (0.2 − 0.02)

O_2 balance: $n_2 = 1 \times 0.80 \times 0.21 - 0.18 \times 0.5$

$= 0.0780$ mol O_2

N_2 balance: $n_3 = 1 \times 0.80 \times 0.79 = 0.632$ mol N_2

So, the first thing that we can do or in fact before that you possibly have already done the degree of freedom analysis and you has realized that this problem can be solvable. Now if we start with the 90% conversion because the unreacted or the remaining of NO would be with the product stream which is n_1, if we look at this that 90% conversion is happening our basis of calculation is 1 mole of the feed.

So, the thing that we have here is the n1 and here the amount that we are feeding to the system we have to find out that the amount of the gas mixture, the composition of the gas mixture and the final pressure that we have in the in the system if the conversion is of 90%. So, here we have 90% conversion that means 10% is remaining which is 0.10 of the amount of NO fed to the system the basis of calculation here we have as 1 mole of the feed in 1 mole we have 20% NO which means we have 0.2 moles of NO.

Out of which 10% is remaining this is the remaining amount which is the n1 that means we have 0.020 mole of NO that is leaving the system unreacted the amount reacted is 1 – 0.02 which is 0.18 sorry it is it is basically 0.2 moles minus this is 0.18 because we have 0.2 moles of NO in the feed. So, this is the NO amount that has been reacted in the system now if we now do the O_2 balance what we have see the point I mentioned or you can realize here this is a single reaction involved.

So, either you do it by the molecular species balance or the atomic species balance it would be relatively straight forward in case of multiple reactions it is always recommended that we go by the atomic species balance. So, here since it is a single reaction lets go with the molecular species balance you can try it with the atomic species balance. So, here we have O_2 balance. So, n_2 is the amount that is leaving the system.

So, we have input that we have is equals to output plus that the amount that is being consumed. So, that means output is equals to input minus the consumption. The input is we have 80% of air in which we have 21% of oxygen and the total mole is 1. So, 0.8×0.21 is the input amount of the oxygen this is subtracted by the amount it is consumed. The amount of consumption we find it by the stoichiometry is that 1 mole of NO requires 0.5 mole of oxygen for its conversion, we have seen how much mole of NO has reacted.

So, this much mole multiplied by 0.5 is the amount of oxygen consumption if we do this calculation we find that n_2 value is 0.0780 mole of oxygen. So, which means n_1 and n_2 are now known. Then we do the nitrogen balance or in fact the nitrogen balance this we could have done it earlier because this nitrogen is inert in this case because nitrogen the molecular species nitrogen is not reacting with anything.

So, the amount of nitrogen that will come out is the amount that it goes in, which is the 80% of 1 mole because the basis of calculation is 1 mole of the feed multiplied by 0.79 or the 79% of this air. So, we can easily find out what is n_3. So, which means now we know what is n_3. n_1, n_2 and n_3 these three are now known to us. The next step we find what is n_4 because we have to calculate what is the composition of the output stream. So, n_4 that means we have to do the NO_2 balance.

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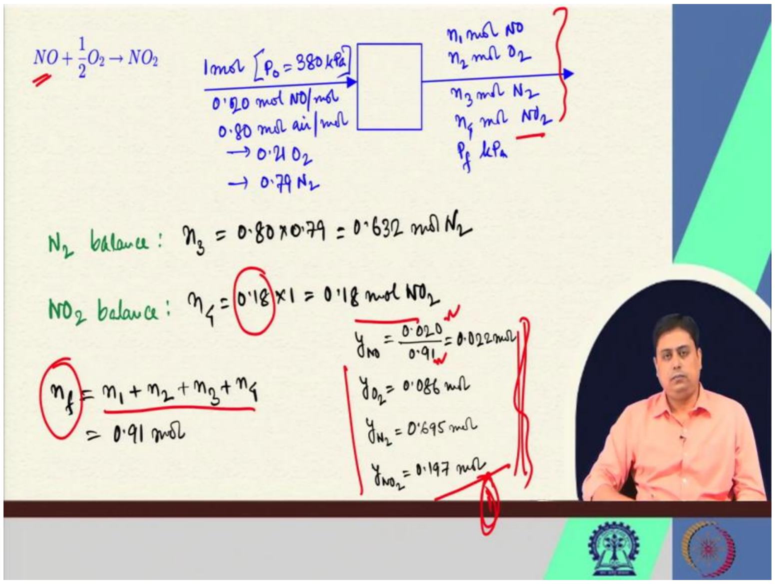

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

1 mol $[P_0 = 380 \text{ kPa}]$

0.20 mol NO/mol

0.80 mol air/mol

→ 0.21 O_2

→ 0.79 N_2

n_1 mol NO

n_2 mol O_2

n_3 mol N_2

n_4 mol NO_2

P_f kPa

N_2 balance : $n_3 = 0.80 \times 0.79 = 0.632$ mol N_2

NO_2 balance : $n_4 = 0.18 \times 1 = 0.18$ mol NO_2

$n_f = n_1 + n_2 + n_3 + n_4$

$= 0.91$ mol

$y_{NO} = \frac{0.020}{0.91} = 0.022$ mol

$y_{O_2} = 0.086$ mol

$y_{N_2} = 0.695$ mol

$y_{NO_2} = 0.197$ mol

Now here once we do the NO_2 balance it is basically the amount of NO itself because 1 mole of NO generates 1 mole of NO_2 we have seen how much mole of NO is reacting which is 0.18 mole of NO was reacting here NO reacted. So, this much mole of NO_2 would be generated which will go out of the system that means now we have all these values. So, we can find out what is the total number of moles.

Once we find out the total number of moles by the summation of n_1 to n_4 we can easily find out what would be the fractions the mole fractions of those the respective amount divided by the total mole the respective mole of the component divided by the total mole. This would give us the mole fraction or the molar composition of the output stream. To cross check the solution you can add all these fractions and you check that the value the total number of moles because the summation of the fractions should be equals to 1.

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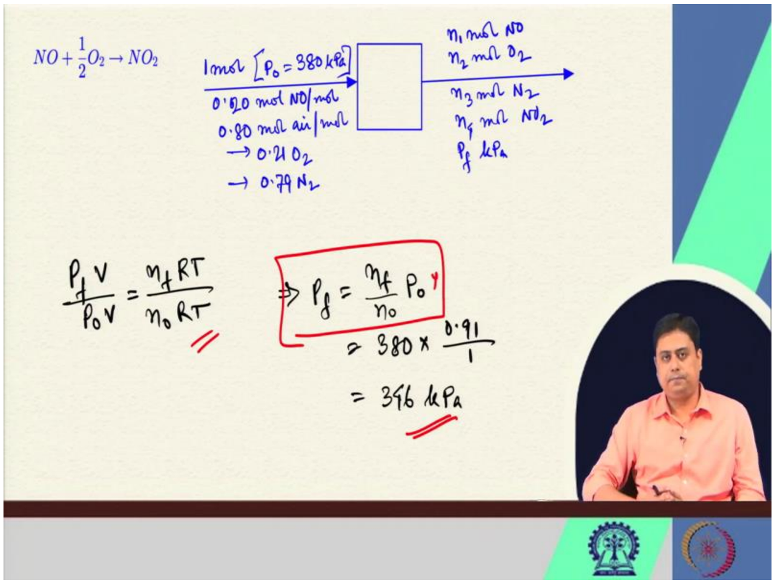

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

$$\frac{P_f V}{P_0 V} = \frac{n_f RT}{n_0 RT}$$

$$\Rightarrow \boxed{P_f = \frac{n_f}{n_0} P_0}$$

$$= 380 \times \frac{0.91}{1}$$

$$= 346 \text{ kPa}$$

So, once this is known we have the second part the first part asks assuming ideal gas behaviour determine the composition of the mixture the component mole fractions this we have calculated now the final pressure if the conversion is 90%. So, we have to now calculate, what is the final pressure because of this amount of moles to be there. So, we know that PV = nRT it is following the ideal gas law in both the condition that is the initial which is P_0 and the final which is coming out of the stream.

The number of moles here we have seen is changing the temperature remain constant because it is isothermal batch reactor universal gas constant remains always constant the volume remain constant here and that is why the moles has changed due to the change in pressure. So, if we divide these 2 expressions we basically get this relation that P final = number of moles at the outlet / the number of moles that goes in the system × the initial pressure.

This is the application of the ideal gas behaviour in this problem to find out what is the final pressure. I hope this is becoming clearer to you that how we are applying the knowledge of this ideal gas behaviour the conversion of the volume and number of moles etc. in the problem that we will solve we have solved in the material balance part. And till now we are dealing with a single phase system that is either purely liquid or purely gaseous state.

The focus here is mainly on the gaseous part because its inherent nature and the attractive calculations that we can do based on the ideal gas behaviour. There are certain or several real gases that do not follow the ideal gas behaviour. For those you have different equation of state. So, you have in those cases different equations of state that means again equation of state provides us the relation between molar amount its volume with the temperature and pressure.

Then those non-ideal gases or the real gases will not discuss here that would be dealt in your forth coming courses.

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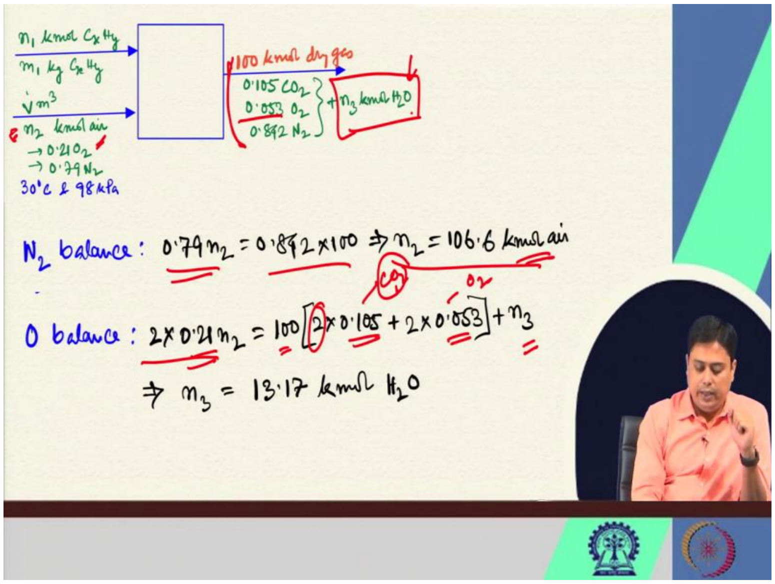

N_2 balance : $0.79 n_2 = 0.892 \times 100 \Rightarrow n_2 = 106.6$ kmol air

O balance : $2 \times 0.21 n_2 = 100 [2 \times 0.105 + 2 \times 0.053] + n_3$

$\Rightarrow n_3 = 13.17$ kmol H_2O

Now say we have another problem like the combustion one that we solved that we did not know what was the fuel and we speculated what could be the composition of the fuel from our calculation. So, once such similar problem here now we are augmenting that with this ideal gas behaviour relations. So, here we have an unknown fuel say C_xH_y ; x and y are unknown is burnt with excess air.

The analysis of the product of this gas gives the following results on a moisture free basis that means on dry basis analysis which is 10.5 V/V or the volume fraction or the volume percentage of CO_2, 5.3% of oxygen and the rest nitrogen. We have to determine that, what is the molar ratio of this hydrogen to carbon in the fuel, this r value, where r = y / x and the percentage excess air used in the combustion that also we have to find out.

And the other question is what is the air to fuel ratio if the air is fed at 30°C and 98 kPa. So, similar to the previous problems, we draw the flow chart these are the things that are unknown to us that n1 kmol of C_xH_y which will have m1 kg weight we have to calculate this value that how much air is being fed to the system at this temperature and pressure linked with the second part.

And our basis of calculation here say is 100 kmol of dry gas because this composition is given for this feed or for this stream on a dry basis. So, we write those compositions plus the component water we should not omit this we should not miss this point because eventually here we have hydrocarbons. So the outlet must contain some water because here from the analysis we can clearly see there is complete combustion is happening there is no carbon monoxide.

So, once this problem statement is now understood what we do we start with the say nitrogen balance, now here in the nitrogen balance because it is an inert it is not taking part in the reaction. So, we know how much nitrogen is going out that is 100 × 0.842 and the input amount is 79% of this much of air that is n_2 kmol of air. So, quickly we can find out what is n_2 this is the kmol of air that is going into the system.

Then we go with the atomic oxygen balance because here we are applying the atomic species balance. The atomic species balance helps us in simply writing the input is equals to output without considering the consumptions generations and all these things. So, what we have here, Here we have this much amount of O_2 in the input it is 21% of air is the O_2. Now 1 mole of O_2 consists of 2 moles of atomic oxygen.

Similarly in the output we have 100 moles of the total stream in which we have 10.5% or 0.105 moles of CO_2 and in this CO_2 we can see there is 2 atomic oxygen 2 moles of atomic oxygen 1 mole of CO_2 and similarly for the oxygen part this is for the oxygen part and we have atomic oxygen from water as well 1 mole of water consists of 1 mole of atomic oxygen. So, n_3, n_2 we have calculated here. So, n_3 is now known to us after simple substitution.

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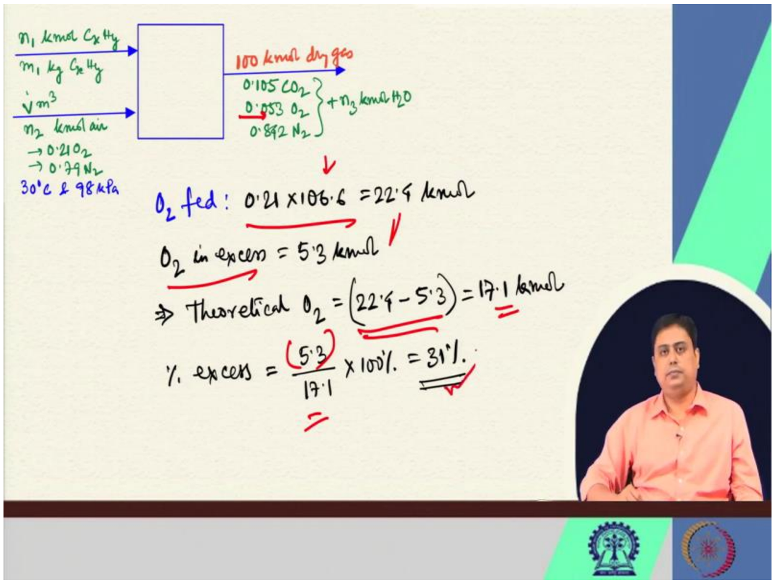

O_2 fed : $0.21 \times 106.6 = 22.4$ kmol

O_2 in excess = 5.3 kmol

$\Rightarrow$ Theoretical $O_2 = (22.4 - 5.3) = 17.1$ kmol

$\%$ excess $= \frac{(5.3)}{17.1} \times 100\% = 31\%$.

Once this is done the other 2 independent species balance again I assume that you have done the degree of freedom analysis. So, the other 2 balance independent balance we can write is C and H the carbon and hydrogen. Now here carbon is fed as the $n_1 \times x$ there is no other source than it and in the output it is only with the carbon dioxide which is 100×0.105 that means 10.5. So, n_{1x} is these values both are unknown.

Similarly for H atomic hydrogen balance we can write n_{1y} is equals to $2n_3$ because 1 mole of water consist 2 moles of atomic hydrogen $2n_3$, n_3 we have calculated in the last calculation. So we can write n_{1y} as this value 2 times of that. So, what we have here in this 2 equation n_{1x} is something n_{1y} is something our desired goal is y / x. So, we divide these 2 expression and we find out what is y / x.

So, this is first answer the second one is that the amount of O_2 fed to the system it is this value that is 0.21 n_2 this was known the excess O_2 is the amount that is leaving out from the system which is 5.3 kmol. So, that means the theoretical oxygen that is required is the difference of these 2 that means the percentage excess is basically the excess amount / the theoretical requirement × 100%, which is 31%. So second part is also done.

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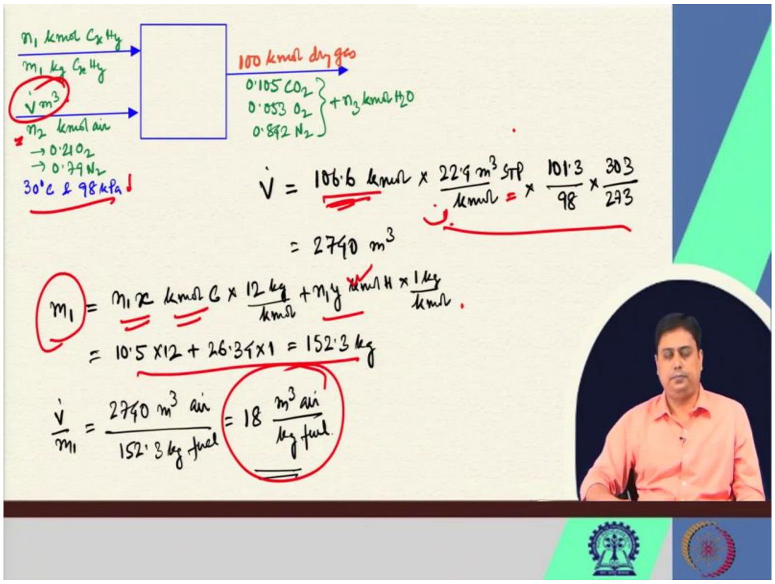

$$\dot{V} = 106.6 \text{ kmol} \times \frac{22.4 \text{ m}^3 \text{ STP}}{\text{kmol}} \times \frac{101.3}{98} \times \frac{303}{273}$$

$$= 2740 \text{ m}^3$$

$$m_1 = n_1 x \text{ kmol C} \times \frac{12 \text{ kg}}{\text{kmol}} + n_1 y \text{ kmol H} \times \frac{1 \text{ kg}}{\text{kmol}}$$

$$= 10.5 \times 12 + 26.34 \times 1 = 152.3 \text{ kg}$$

$$\frac{\dot{V}}{m_1} = \frac{2740 \text{ m}^3 \text{ air}}{152.3 \text{ kg fuel}} = 18 \frac{\text{m}^3 \text{ air}}{\text{kg fuel}}$$

The third part it is required that we convert the volume to a desired temperature and pressure. So, what we have the number of moles going out of the system or here the n_2. We are now calculating the V· based on the n_2 and we know we converted that to the volume at STP by this known relation and then this volume at this temperature and pressure we are converting to this temperature and pressure from the STP which is 0 degree centigrade or 273 K and 101.3 kPa this conversions we have discussed now couple of times.

So, we get the value of the V·. Now we calculate what is the mass or this ratio that the mass of the fuel because it is also necessary that we calculate how much air is needed per kg of the fuel. Now the mass is n_{1x} kmol of C carbon and this 1 mole of or kmol of carbon is of 12 kg. Similarly n_y ×1 because hydrogen is 1kmol of hydrogen is atomic hydrogen is 1 kg. So, we basically get the value of the mass of the fuel we divide these 2 to get the volume that is necessary the air volume that is necessary per kg of the fuel burnt.

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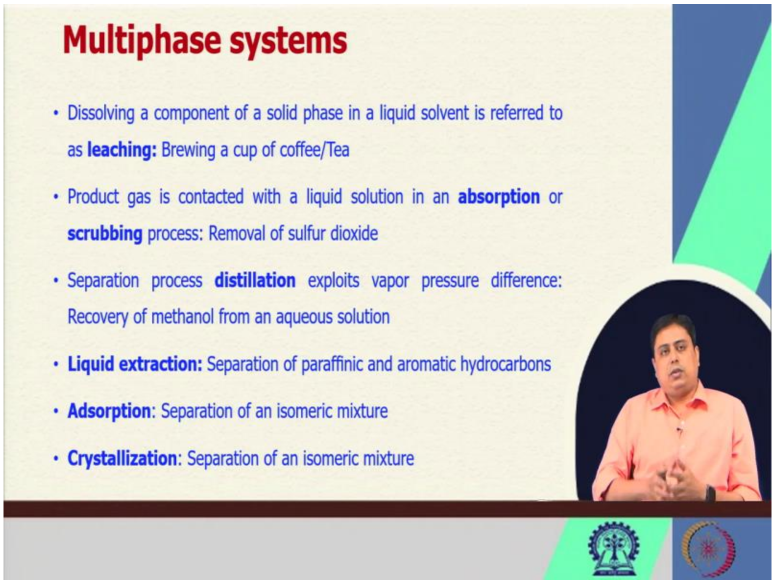

Multiphase systems

- Dissolving a component of a solid phase in a liquid solvent is referred to as **leaching:** Brewing a cup of coffee/Tea
- Product gas is contacted with a liquid solution in an **absorption** or **scrubbing** process: Removal of sulfur dioxide
- Separation process **distillation** exploits vapor pressure difference: Recovery of methanol from an aqueous solution
- **Liquid extraction:** Separation of paraffinic and aromatic hydrocarbons
- **Adsorption**: Separation of an isomeric mixture
- **Crystallization**: Separation of an isomeric mixture

Now coming to the concept of the multiphase system that I will briefly introduce in next couple of minutes because these concepts you will see or will be discussed in the forthcoming courses as well as in the next module starting with the energy balance. Now there are several practical examples for example leaching, absorption, distillation, liquid extraction, adsorption crystallization these terms you will hear as the unit operations having in a system.

So, for example that dissolving the component of a solid phase in liquid solvent is the process called leaching. And this example is the brewing a cup of coffee or tea or say a tea bag dipped into a hot water. It is a solid component that dissolves in the liquid. So, there that means we have solid particles and the liquid. So, this is a multiphase system when the product gas is contacted with a liquid solution absorption happens or a scrubbing process where the absorption happens for example removal of sulphur dioxide or carbon dioxide in a appropriate solvent.

So, there the gas and the liquid comes in contact and forms a multiphase system the separation process in distillation we have the vapour pressure difference. For example recovery of methanol from its aqueous part the extraction the liquid extractions are done for the separation of paraffinic and aromatic hydrocarbons similarly there are adsorption and crystallizations for some specific applications are there.

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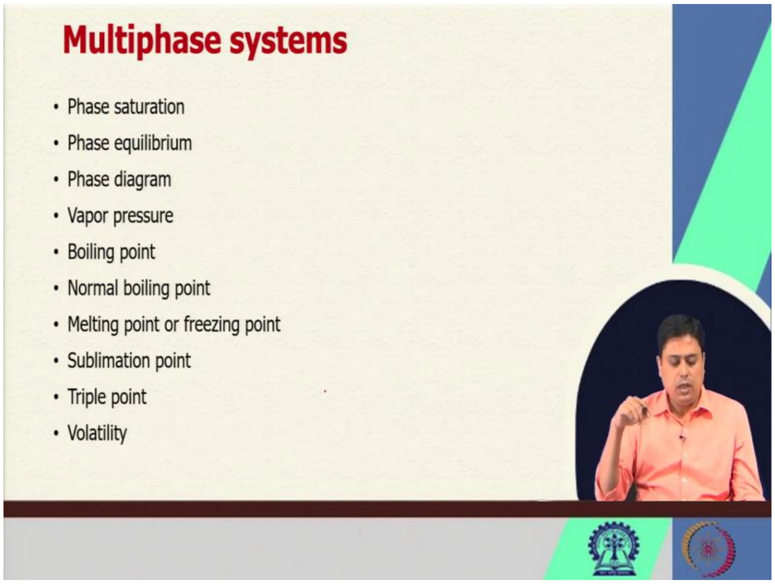

Multiphase systems

- Phase saturation
- Phase equilibrium
- Phase diagram
- Vapor pressure
- Boiling point
- Normal boiling point
- Melting point or freezing point
- Sublimation point
- Triple point
- Volatility

Now here you will hear couple of terms like phase saturation, phase equilibrium, phase diagram, vapour pressure, boiling point etc. So, the thing that happens is that when a phase comes in contact with another phase and if those 2 are not in equilibrium then the transfer of one phase happens to the other phase and it reaches at a stage where one phase is saturated with other phase. And the stage where no transfer happens we call that the phase equilibrium there are phase diagrams the phase diagrams helps us for example for water.

So, we have this kind of a phase diagram phase diagram here we have say T in the x axis and typically the phase diagram consist pressure on the y axis. Now at different temperature and pressure you realize the water would be in certain form either its solid, gas or the liquid form. So, typically at say low temperature and low pressure in this region so, this kind of a region. So, here you have say solid water as solid this region there would be the vapour and here you find the water as liquid.

So, depending on the temperature and pressure you find different state of water this is called the phase diagram that you find water in different phases and these solid lines are basically the equilibrium lines. So, this line this one particular we can say this is the solid vapour equilibrium, this is the liquid solid equilibrium curve, and this is the liquid vapour or vapour liquid equilibrium curve. Depending on which equilibrium curve you are there are different vapor pressure and temperatures you find.

So, for example if you are on say vapour liquid equilibrium curve on this line ok on these lines the water may exist in both the phases it coexist, both phases coexist. So if at this temperature the pressure is called the vapour pressure of water at this temperature. At this temperature this at this pressure water has this boiling point when it falls on this line or say specifically the normal boiling point.

So, when the pressure is one atmosphere we typically call that as normal boiling point, any boiling point when the pressure is at one atmosphere. So, similarly when you are on say the solid liquid equilibrium curve this one this temperature can be called at that pressure as either melting or the freezing point based on from which side you are coming and in this solid vapour line you have the sublimation point that at that pressure this is the sublimation point.

So if you come across from solid and goes with a constant pressure with the temperature you would have the solid immediately goes into the vapour without becoming liquid where the three phases coexist we call that as the triple point. This vapour pressure is basically a measure of volatility the volatility is basically the species it gives us a measure that how much it tends to transfer from say the liquid or solid to its vapour state.

The more volatile matter or the substance if the vapour pressure is basically the measure of this volatility. So, highly volatile matter is more prone or more likely to be found in the vapor phase and the less volatile matter would be in the condensed phase that is the liquid or the solid phase.

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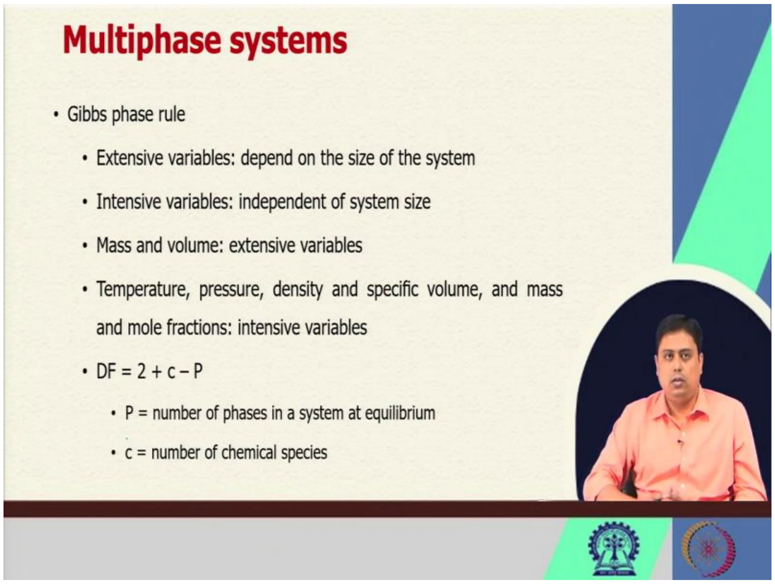

Multiphase systems

- Gibbs phase rule
  - Extensive variables: depend on the size of the system
  - Intensive variables: independent of system size
  - Mass and volume: extensive variables
  - Temperature, pressure, density and specific volume, and mass and mole fractions: intensive variables
  - $DF = 2 + c - P$
    - P = number of phases in a system at equilibrium
    - c = number of chemical species

So, you will hear this terms and the other thing that is important is the Gibbs phase rule and if we try to understand the Gibbs phase rule 2 things also comes in which you are perhaps ever is the extensive variables and intensive variables. The system variables by which we define our working condition say for example you are given a mixture of a certain system and you have to tell this to someone that how you made it or what is the condition of that you have to specify some system variable that it is at this parameter this temperature this pressure this is the mole fractions of it.

So, then other one can replicate the same thing. So, the necessary parameters or the variables are classified in these intensive and extensive variables because whatever you are mentioning or indicating those variables all those variables are not basically independent if you fix something the other variables would automatically be fixed. So, when a variable depends on the size of the system it is called the extensive variable and when it is not it is the intensive variables.

So, mass volume these are extensive variable it depends on the size of the system but the temperature, pressure, density, specific volume, mass and mole fractions these are all intensive variables it does not depend on the size of the system. So, the number of intensive variable that you must specify in order to tell a system that is the degree of freedom here by the Gibbs phase rule it is 2 + C – P which is P where the P is the number of phases in a system at equilibrium and C is the number of chemical species that are involved in the multiphase system.

So, this degree of freedom is basically analogous to what we have done in the material balance while calculating it or understanding a problem there we realize the degree of freedom is basically the number of the system that whether it tells us whether the system is solvable or not or whether the information the number of variables or the number of known parameters that are given are sufficient to solve the problem or not.

So, similarly here the degree of freedom would tell us from the Gibbs phase rule that those many intensive variables that we must specify in order to define a system. So, for example say if I quickly give you an example that how it works say pure liquid water, in pure liquid water we have phase one that only one phase is there. We have component only one component. So, the degree of freedom by Gibbs phase rule it tells that 2 intensive variables must be specified in order to state the system that contains pure liquid water that is the temperature and the pressure.

So, once these variables if you say specify I mean this is the example the temperature and pressures the other 2 can be also there but say for example if you specify temperature and pressure for this system that contains pure liquid water you need not specify any other parameter because those others will be automatically defined. Say the point is that say you have a vapour liquid mixture of acetone and methyl ethyl ketone such kind of a thing.

So, there you have basically 2 phases you have 2 components. So, degree of freedom there is also 2. So, that means 2 variables intensive variables must be mentioned in order to fix the state of the system that if you state temperature and pressure the other all independent intensive variables would be automatically fixed you cannot change those. So based on these concepts I will conclude my section or conclude my lectures here.

Because the next module starting with the energy balance would be taken by Professor Rabibrata Mukherjee. I hope you had learnt significant portions on the material balance. If you have any questions please feel free to ask through different forums that we have opened and we wish you a very good luck with the course. Thank you for your attention.