Chemical Reaction Engineering

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Lecture No. # 08

Problem Solving: Thermodynamics and Kinetics

Friends, let us take a pause and summarize what we have done in this what I call as a first module in our reaction engineering course. And this essentially refers to thermodynamics and kinetics. So what we are going to do today is briefly look at what we have done so far, and then look about few problems and solve it and see how to solve the such problem. These are typical problems of course, one cannot cover up all the problems or all kind of problems, but these are few representative problems, which you may come across in your reaction engineering practice.

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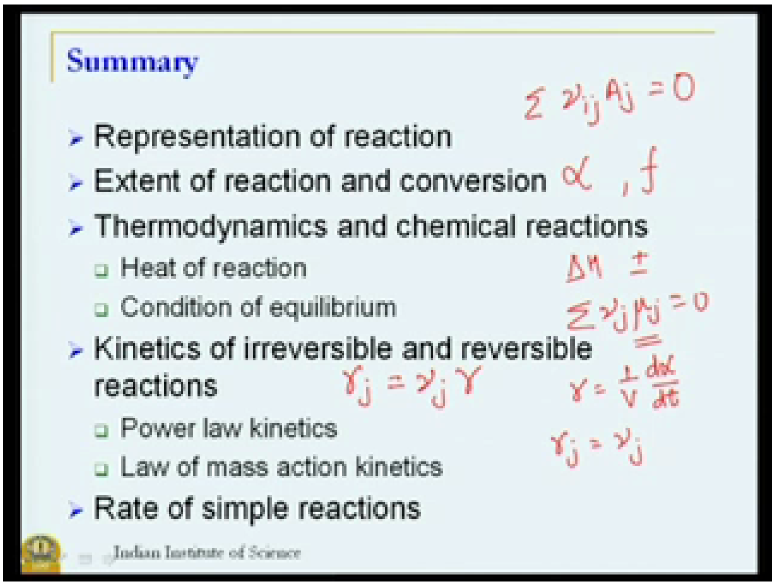

Summary

$\Sigma \nu_{ij} A_j = 0$

- Representation of reaction
- Extent of reaction and conversion α , f
- Thermodynamics and chemical reactions
  - Heat of reaction ΔH $\pm$
  - Condition of equilibrium $\underline{\underline{\Sigma \nu_j \mu_j = 0}}$
- Kinetics of irreversible and reversible reactions $r_j = \nu_j r$ $r = \frac{1}{V}\frac{d\alpha}{dt}$
  - Power law kinetics $r_j = \nu_j$
  - Law of mass action kinetics
- Rate of simple reactions

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So, we started our discussion after a brief introduction by looking at how do we represent the reaction, and we said we will define the stoichiometric matrix, so that when we have large number of reactions or let us say, and there are n species participating in these reactions and how do we represent these reactions. So, we said that we will define the stoichiometric coefficient nu i j as the stoichiometric coefficient of species j in the i th reaction, and then represent the i th reaction as summation nu i j A j equal to 0. And the idea here is that we now can denote whether the the species is reactant or product by looking at the sign of these stoichiometric coefficient, if it is negative, then we say that it is a reactant; if it is positive then we said it is a it is a product.

We then moved on to look about how do we measure the progress of reaction and we define two quantities here namely the extent of reaction alpha and the conversion f. The prime difference between these two quantities is that the extent of reaction alpha is tied down to the reaction whereas, the conversion f or at times we have used notation x also is tied down to the species. So if there are r reactions for example, we have r extent of reactions alpha 1 alpha 2 and so on. Whereas, when it comes to conversion it is tied down to the to the species and we cannot define conversion for all species. Because if we have started your reaction with non stoichiometric quantities of reactants and products then typically there will be one reactant, which will be limiting or which will get consumed first and once it is consumed reaction cannot proceed further.

So we define the conversion using what we call stoichiometrically limiting species. We also talked about thermodynamics and chemical reactions, why thermodynamics is important. First of all it tells us about the heat changes that accompany a reaction. So we can calculate the heat of reaction as summation of nu j A j that is partial molar enthalpies s j and nu j our stoichiometric coefficient. This tells us for example, whether heat is going to be liberated in our reaction or heat is going to be absorbed from the reacting system. So whether we have a exothermic reaction or we have a endothermic reaction.

So the sign of delta H the heat of reaction positive, endothermic reaction negative and exothermic reaction. We also talked about the condition of equilibrium because this is an important quantity. Because it tells you how far you can drive your reaction without how far can you drive your reaction at given operating conditions. So we for example, talked about the condition of equilibrium which we can write as summation nu j mu j equal to zero for a single reaction and similar thing summation nu i j mu j equal to 0 for any i th reaction nu j as before are our stoichiometric coefficient. And mu j is nothing but our partial molar free energy or the chemical potential and we spend little bit of time on how we define this chemical potential depending on whether the reaction is a gas phase reaction or a liquid phase reaction or a gas liquid reaction or gas solid reaction and so on.

The condition of equilibrium remains the same but how we define our chemical potential differs, when we have different different phases, subsequent to this we came to the kinetics of the of the reaction whether it is a irreversible reaction or whether it is a reversible reaction. So the idea here is to define the rate of reaction and the rate of reaction we define saying that in a closed system; that is no exchange of mass with the with the surrounding so like a batch reactor. For example, so in a close system the rate of reaction r is given by one over v d alpha dt, where v is the volume of the reacting reacting mixture and alpha is the extent of reaction as we had define earlier.

The property of extent of reaction namely it has a value zero at the beginning because reaction is not progressed at all too and upper limit of either one or whatever is dictated by the equilibrium of the species. So alpha e that is what we find from our condition of equilibrium whatever may be the upper limit the extent of reaction is always increasing. And at base it can reach a saturation value either when the reactants is completely consumed or the equilibrium is reached which means that d alpha dt is always positive and therefore, we define our intrinsic rate of reaction as a positive quantity.

This is again tied down to the reaction so the change of species moles or rate of change of species mole r j is related to this r as nu j into nu j into alpha. So for example, if r j is the rate of change of j species then we call it equal to nu j into r sorry nu j into r that is that is our reaction rate or intrinsic reaction rate as we have we have defined. Our empirically there are several ways of defining reaction rate so power law kinetics or law of mass action kinetics and then there are other forms that one could have but these are the common forms that are used.

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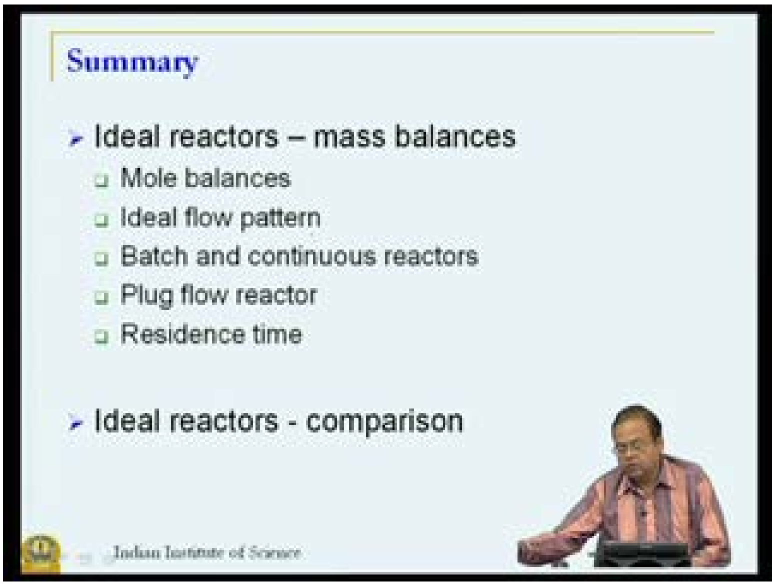

Summary

- Ideal reactors – mass balances
  - Mole balances
  - Ideal flow pattern
  - Batch and continuous reactors
  - Plug flow reactor
  - Residence time
- Ideal reactors - comparison

We also then summarized our discussion or completed our discussion by looking at ideal reactors; that is what is ideal about them namely the flow conditions with perfect mixing as a as in stirred tank reactor or no mixing in the axial direction or in the direction of the flow as in the plug flow reactor. So we talked about this flow patterns then batch and continuous reactors, semi batch reactors and the idea of residence time, space velocity and so on towards the end.

We also looked at how we can compare the performance of two reactors namely stirred tank reactor and plug flow reactor and came to the conclusion. For reactions, which follow power law kinetics with power being a positive number plug flow reactor will always give you better conversions than the same volume but operated in a stirred reactor manner. But there are situations where stirred reactor will give you better conversions both isothermal as well as non isothermal.

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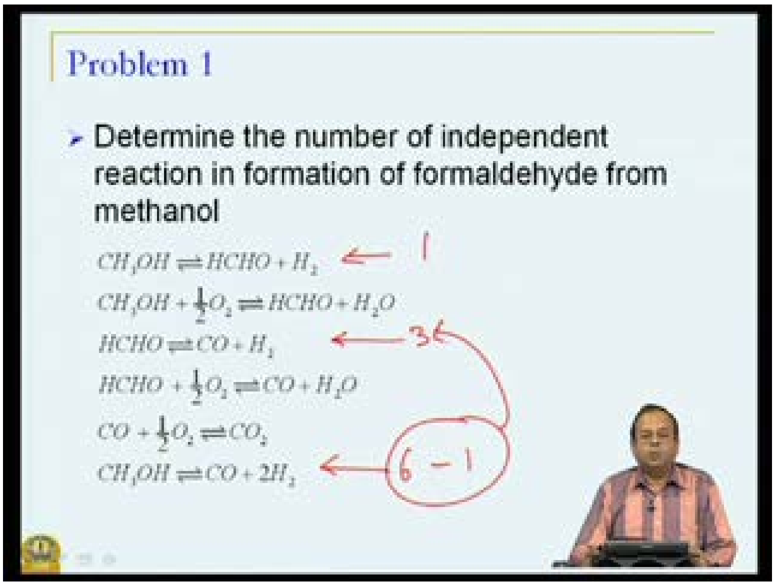

Problem 1

- Determine the number of independent reaction in formation of formaldehyde from methanol

$$CH_3OH \rightleftharpoons HCHO + H_2 \longleftarrow 1$$
$$CH_3OH + \frac{1}{2}O_2 \rightleftharpoons HCHO + H_2O$$
$$HCHO \rightleftharpoons CO + H_2 \longleftarrow 3$$
$$HCHO + \frac{1}{2}O_2 \rightleftharpoons CO + H_2O$$
$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$
$$CH_3OH \rightleftharpoons CO + 2H_2 \longleftarrow (6-1)$$

So with this brief summary now let us look at few of the problems that one can encounter and will take few typical problems and see how we can solve them. Now before we go to the actual problem I want to emphasis that why solving the problem I have seen tendency of students the moment they get papers from their examiners they start writing something; I do not know what they start writing and I think this is little dangerous because it is always helpful to look at the paper or look at the question and try to play a game in your mind to figure out what is the question.

What is it that I am trying to find out? Often one finds that what appears to be question as written in black and white is not really the question. So one has to look at is there any other meaning behind what is what is a question asked and I will elaborate on that as we as we go along. The second thing that if at all you want to writing I think it is always better to write all the information that you have through your problem in a concise manner that means what is that data. The third thing that you need to think before start writing is which tools and knowledge based, am I going to use, does this problem refer to thermodynamics or kinetics or reactor design isothermal non isothermal?

So try starting your solving your problem by organizing your ideas before starting some equation and trying to get something without having a clear idea as to what is the objective. So let us take our first problem and it says that its simple there are set of reactions given six of them and we are supposed to find independent number of reactions in the formation of formaldehyde from methanol. So where main reaction may be methanol decomposition or dehydrogenation to formaldehyde and hydrogen but there are several reactions that can occur.

Now remember when we talked about thermodynamics or kinetics or stoichiometry for that matter we always talked about independent reactions and therefore, the first step that we need to do in solving in a reaction engineering problem is to see whether set the of reactions that are given are independent or not. The moment is question is posed what comes to mind how can I find is independent reactions, I can start looking at these reactions and then see whether any combination of any two reaction gives me third reaction and and so on. In fact if you look at this set of reaction you can after little little practice or you are smart enough you will realize that may reaction three reaction three is actually my reaction six minus my reaction one.

So this is what gives me my reaction three. So these are not independent reactions. So that is one way of solving this problem but that is possible only when you have few reactions and even in this case when we have only six reaction although the first one is easy to find, second one is not that easy. So what is it that that we need to find. What knowledge based we need to need to use? We need to use the fact that we can represent these reactions as a stoichiometric matrix and then look at the rank of this stoichiometric matrix which gives me what are the independent reactions.

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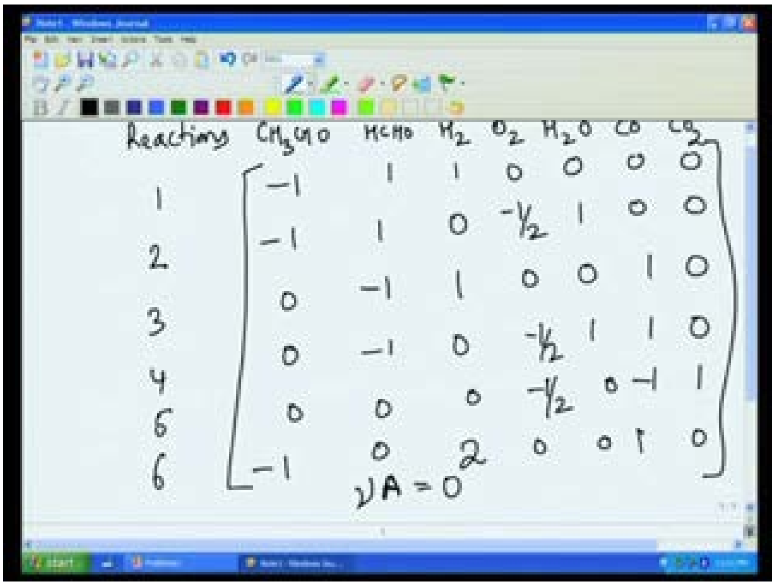

$$\begin{array}{c|ccccccc} \text{Reactions} & CH_3OH & HCHO & H_2 & O_2 & H_2O & CO & CO_2 \\ 1 & -1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 2 & -1 & 1 & 0 & -1/2 & 1 & 0 & 0 \\ 3 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 4 & 0 & -1 & 0 & -1/2 & 1 & 1 & 0 \\ 6 & 0 & 0 & 0 & -1/2 & 0 & -1 & 1 \\ 6 & -1 & 0 & 2 & 0 & 0 & 1 & 0 \end{array}$$

$$\nu A = 0$$

So let us try doing that by write the stoichiometric matrix. So let us say we start with our first reaction namely methanol gives formaldehyde plus hydrogen. Now if you examine this reaction set you will see that there are six reactions. So let us say that we put reactions over here one two three four five and six and let us try write start writing the species that are involved in this reaction. So what are the that species that are involved so we can see here its methanol, formaldehyde, hydrogen, oxygen, water, carbon monoxide, carbon dioxide are the are the species.

So as a column let us write those species so methanol, formaldehyde, hydrogen, oxygen, water, carbon monoxide and carbon dioxide. So for each reaction one at a time we are going to represent the stoichiometric coefficients of these species in a given reaction. So if you look at the first reaction if you look at the first reaction my methanol is a reactant with a stoichiometric coefficient one. So it will be as per my convention minus one because that is a reactant. Formaldehyde being product as plus one and hydrogen also being product as plus one and there are no other species.

So I will write my first entry as minus 1 1 1 0 0 0 0, if I do the same thing for the second reaction and so on. I will get this particular stoichiometric matrix that is all I am doing is I am looking at one reaction at a time. And seeing how what is the stoichiometric coefficient putting a minus sign if it is a reactant and putting a plus sign if it is a product. So this is my stoichiometric matrix nu and my reaction reactions are mu i j aj equal to zero or if i represent vector a as A 1 into A 3 a seven species here, then this represents my reaction set.

So we will represent these reactions as nu A equal to zero. So our next task is to find out the number of independent reactions and what those reactions are. Now just looking at those reactions or looking at these looking at these matrix; we said that my reaction three is six minus one is my third reaction and you can actually do this exercise and you will see that the row three is obtained by subtracting respective elements of row six and row one.

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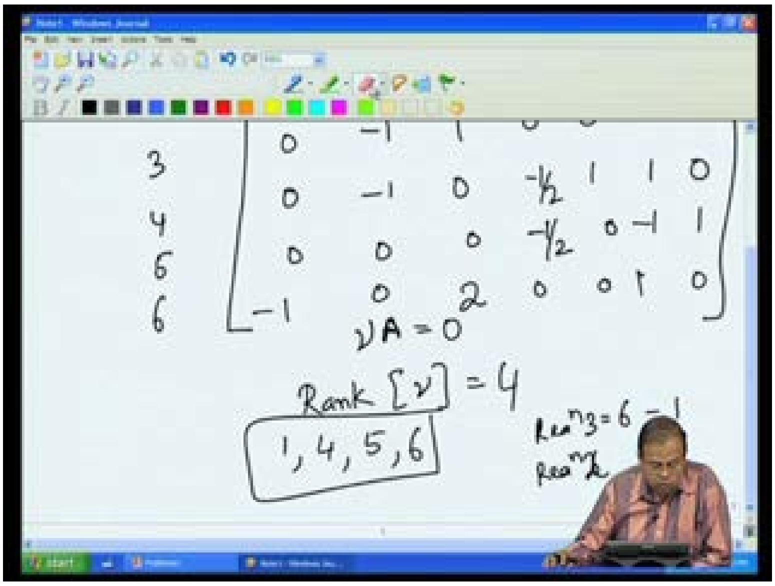

But that is not an ideal way because if you have hundreds of reactions how will you know. So what is the next thing I have to find the rank of this matrix and the rank it turns out in this particular case we can of course, use and there is no reason why we should not use any available software such as matlab mathematic; or any other program that you yourself have written to find the rank of this matrix and it turns out the rank of our matrix nu is 4 and we can take any four reactions.

So 1, 4, 5, 6 any four but we should be careful and with these are my independent reactions and then as I said earlier my reaction three is actually 6 minus 1 and my reaction six once again reaction six is actually two times one plus four. So if I can choose one four five six as my independent reactions I have satisfied the requirement. My reaction two my reaction two I stand corrected my reaction two my reaction two is two two times reaction one plus four minus six, you can go back to that reaction set and see how it works out.

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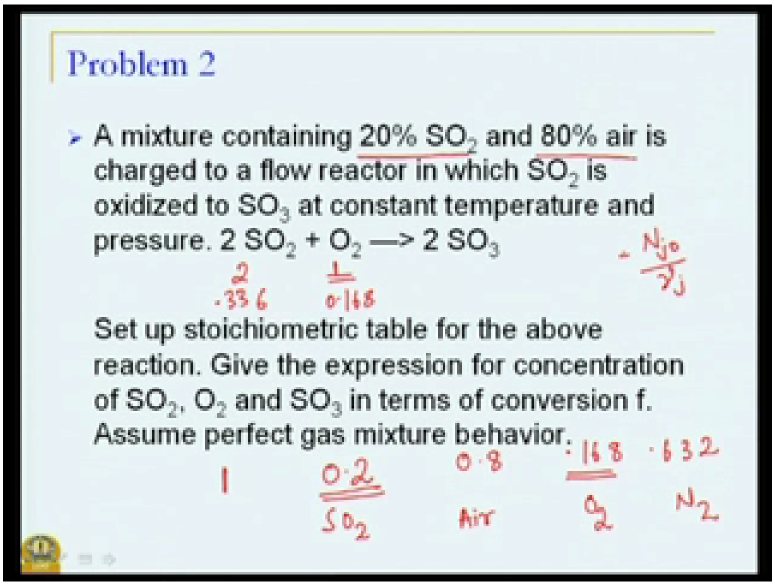

Problem 2

- A mixture containing 20% SO_2 and 80% air is charged to a flow reactor in which SO_2 is oxidized to SO_3 at constant temperature and pressure. $2\ SO_2 + O_2 \longrightarrow 2\ SO_3$

$-\frac{N_{j0}}{\nu_j}$

2 .336

1 0.168

Set up stoichiometric table for the above reaction. Give the expression for concentration of SO_2, O_2 and SO_3 in terms of conversion f. Assume perfect gas mixture behavior.

1

0.2 SO_2

0.8 Air

.168 O_2

.632 N_2

So this is the first problem simple one, we will go in the order in which we covered various various materials. The second problem let me read out the problem statement to you and this is also something we require every now and then even when we are doing reactor design and so on. What is it? It is namely setting up of the stoichiometric taper. So here we have a mixture containing twenty percent SO 2 and eighty percent air is charged to a flow reactor in which sulphur dioxide is oxidized to sulphur trioxide at constant temperature and pressure the reaction is given to us.

So our job is to set up the stoichiometric table for above reaction and we are also expected to give expressions for concentration of SO 2 O 2 SO 3 in terms of conversion conversion f. We will assume perfect gas behaviour. Now this is a straight forward problem except there is a small hitch namely we have being asked to find a concentration expressions in terms of conversion conversion f. Now we know that we define conversion in terms of species, which is chemically chemically limiting or stoichiometrically limiting.

So our first job here would be to find out among SO 2 and O 2 which is the species which is stoichiometrically limiting and unless we do that setting up of this stoichiometric table does not make any sense or it will be incorrect if we choose a wrong species. Because what will happen if we choose a wrong species is that conversion either will go above hundred percent or may become a negative negative value. So how do we find out which is the limiting species and to do that we have been given this particular particular information.

So what is the information that is available to us we know that there is twenty percent SO 2 and eighty percent air in our feed. So either you take it as a molar feed or let us take molar feed so we say that we suppose our molar feed is one mole which actually is not one but it can be anything but if you take one mole as a basis. Then we know that there are 0.2 moles of SO 2 and 0.8 moles of air, which if we now what is our reactant our reactant is not air it is is oxygen.

So air has oxygen and nitrogen so which assuming twenty one percent oxygen I can write this as 0.168 oxygen and the remaining namely if my mathematics is correct will be 0.632 it should add up to 0.8 moles of nitrogen. So what we have is 0.168 moles of oxygen and 0.2 moles of SO 2. So which is which our stoichiometrically limiting limiting species is? In this case what we what we say we will go back our reaction; you know what is the formal way of formal way of doing this that is look at the ratio of minus N j zero by nu j and choose the minimum of this value but it amounts to doing the following.

For every mole of oxygen one mole of oxygen we need two moles of SO 2. So if we had 0.168 moles of moles of oxygen we need double that quantity of SO 2 for complete conversion of oxygen. So that would be so stoichiometrically for 0.168 we need 0.336 moles of moles of SO 2. But how much do we have we have only 0.2 that means SO 2 is our limiting species and we should therefore; define conversion in terms of these limiting species namely SO 2 and then set up our stoichiometric table.

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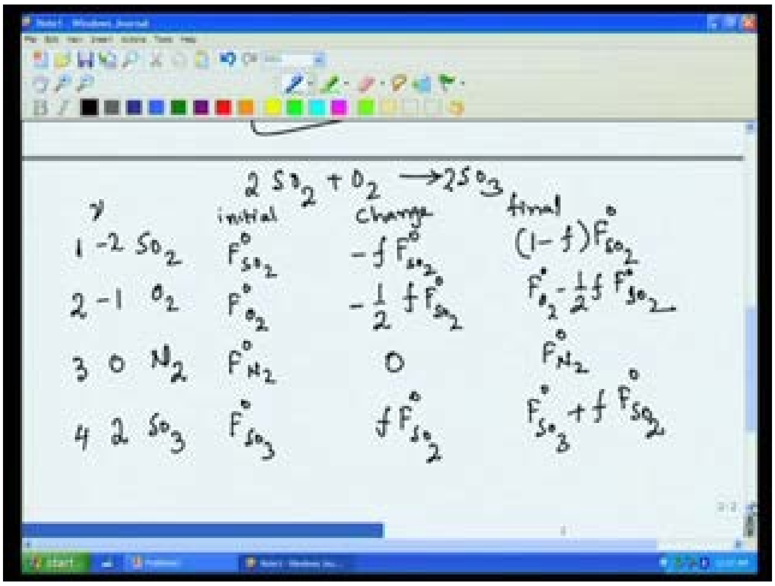

$$2SO_2 + O_2 \rightarrow 2SO_3$$

	ν		initial	change	final
1	-2	SO_2	$F^0_{SO_2}$	$-fF^0_{SO_2}$	$(1-f)F^0_{SO_2}$
2	-1	O_2	$F^0_{O_2}$	$-\frac{1}{2}fF^0_{SO_2}$	$F^0_{O_2}-\frac{1}{2}fF^0_{SO_2}$
3	0	N_2	$F^0_{N_2}$	0	$F^0_{N_2}$
4	2	SO_3	$F^0_{SO_3}$	$fF^0_{SO_2}$	$F^0_{SO_3}+fF^0_{SO_2}$

So, let us try to do that by setting up the stoichiometric table, and by recognizing that this is my reaction. So if I take my species one as SO 2, species two as O 2, species three as N 2, because that is also there species four as SO 3. So, how do we proceed, we say that let us say, so which I will just write here although that is let me try writing it here, initial change and final for all these species. And let us say F naught SO 2 is my initial F naught O 2 F naught N 2 and F naught SO 3 as my initial, and I am going to define my conversion F in terms of SO 2.

So let us say the change is f into F SO 2 zero is how much has changed. So final or whatever is remaining is one minus f into F naught SO 2 that are final are initial plus change. Now for every f into SO F naught SO 2 that has changed how much has oxygen oxygen changed strictly speaking we need to identify my species so I can write here my stoichiometric coefficients nu for each of the species. So that is minus two minus one zero and plus two. So how do we set up the stoichiometric table we said that it is minus nu two by nu one into f into F naught of SO 2.

So that is that is how much it has changed so if we now substitute what is our nu one nu two nu three nu four; if you substitute that I will get here in this particular case I will get one by two. And therefore, this will be F naught of O 2 minus half f F naught of SO 2 nitrogen is not participating; so it remains same as before and for every we use the same formula as as we had written. So this will be minus two by minus two so this will be simply f into F naught of SO 2. So this will be F naught of SO 3 plus f into F naught of SO 2.

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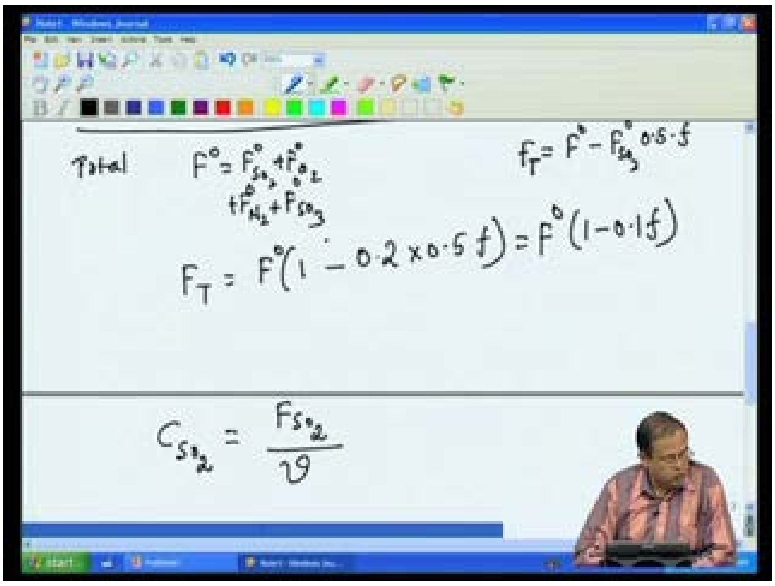

Total

$F^{0} = F^{0}_{SO_2} + F^{0}_{O_2} + F^{0}_{N_2} + F^{0}_{SO_3}$

$F_T = F^{0} - F^{0}_{SO_2}\,0.5\cdot f$

$F_T = F^{0}(1 - 0.2 \times 0.5 f) = F^{0}(1 - 0.1 f)$

$C_{SO_2} = \frac{F_{SO_2}}{\vartheta}$

So I can now write total here it is a total so this if I say it was F naught then this will be F naught SO 2 plus F naught O 2 plus F naught into plus F naught SO 3 and if I do the same thing same thing over here. So I am just going to add up so minus one plus half and you know what needs to be what needs to be done. We will get F T total that is the final one as F naught into one minus point rather if I take a total we will get F naught minus F SO 2 naught into 0.5 into f if you add up all these quantities.

So now we have our stoichiometric stoichiometric quantities so I can take here F T as F naught minus one minus just going to to rearrange this one minus F SO 2 naught by F naught which is 0.5 0.2. So 0.2 into 0.5 into f. And this tells me what is what is my so one thing that we see now is that my total moles is no longer constant. Because there is change in number of moles in the reaction from three moles on the reactant side we are getting two moles on the product side.

So my flow rate is flow rate is changing. So now let us, what is our objective? What is our question? Our question is to get concentration of SO 2 in terms of its conversion. What is concentration? Concentration is the molar flow rate of SO 2 divided by the volumetric flow rate volumetric flow rate v so that is what our concentration concentration is.

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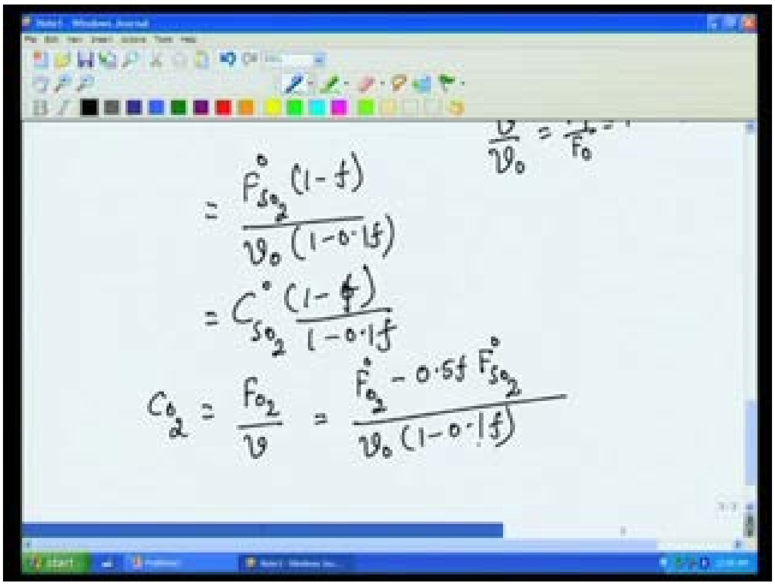

$$\frac{v}{v_0} = \frac{F}{F_0}$$

$$= \frac{F^{\circ}_{SO_2}(1-f)}{v_0(1-0.1f)}$$

$$= C^{\circ}_{SO_2}\frac{(1-f)}{1-0.1f}$$

$$C_{O_2} = \frac{F_{O_2}}{v} = \frac{F^{\circ}_{O_2} - 0.5f\,F^{\circ}_{SO_2}}{v_0(1-0.1f)}$$

We know our molar flow rate in terms of this is my F of SO 2 I know that in terms of conversion but what about volumetric flow rate. Remember we have a gases reaction accompanied by change in number of moles; so if I have now or if I take make use of my ideal gas behaviour, which is what that p into v volumetric flow rate is total number of moles RT. So if I take my pressure and temperature constant then v by v naught is F T by F naught, which from the above equation this equation over here is one minus 0.1 f.

Now let me put F naught of SO 2 into one minus f for F of SO 2 and for v I will put v naught into one minus 0.1 f this two together now gives us. What is f naught of SO 2 by v naught those are all inlet conditions. So this is nothing but concentration of SO 2 at the inlet so minus one minus f divided by one minus 0.1 0.1 f and we can go on doing this for all of them. For example, for concentration of O 2 it will be Fof O 2 divided by v which will be F naught of O 2 minus 0.5 f into F naught of SO 2 divided by v naught into 1 minus 0.1 f.

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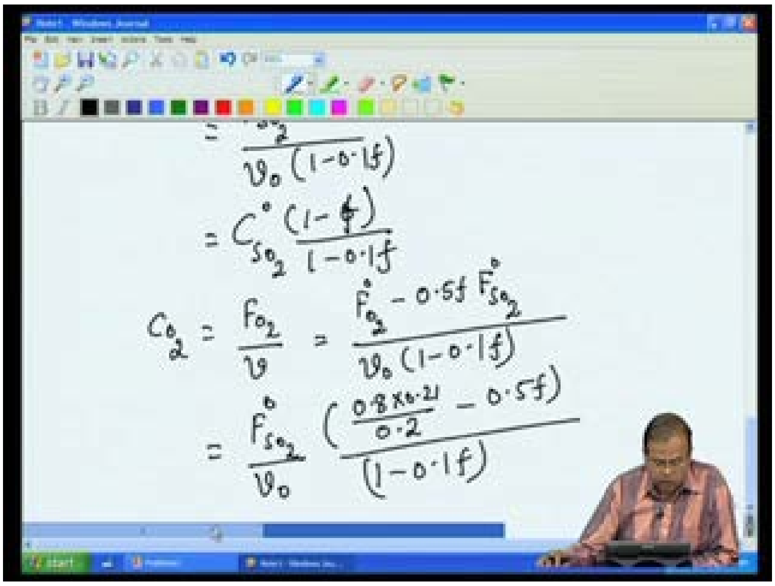

$$= \frac{}{\upsilon_0 (1-0.1f)}$$

$$= C^{\circ}_{SO_2} \frac{(1-f)}{1-0.1f}$$

$$C_{O_2} = \frac{F_{O_2}}{\upsilon} = \frac{F^{\circ}_{O_2} - 0.5f\, F^{\circ}_{SO_2}}{\upsilon_0 (1-0.1f)}$$

$$= \frac{F^{\circ}_{SO_2}}{\upsilon_0} \frac{\left(\frac{0.8 \times 0.21}{0.2} - 0.5f\right)}{(1-0.1f)}$$

Once again in this particular case we can take F naught of SO 2 out as a common factor and then write this as 0.8 divided by 0.8 into 0.21 divided by 0.2 minus 0.5 f divided by one minus 0.1 f. What are this on the top is twenty one percent of air which was eighty percent of the total feet which is oxygen and on the denominator here is 0.2, which is which is my mole fraction of SO 2. So likewise we can we can go and complete complete my my kinetic or my concentration expressions you I leave it to you to try it out for concentration of nitrogen concentration of SO 3 and so on.

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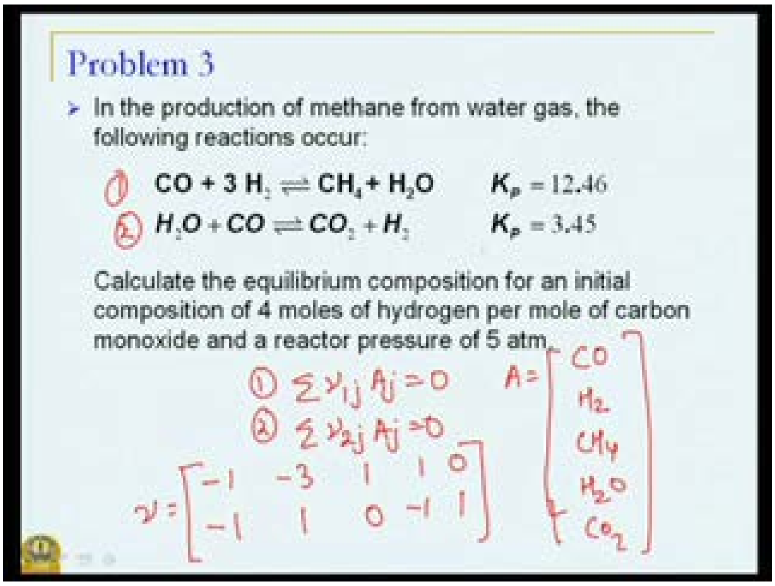

Problem 3

- In the production of methane from water gas, the following reactions occur:

① $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ $K_p = 12.46$

② $H_2O + CO \rightleftharpoons CO_2 + H_2$ $K_p = 3.45$

Calculate the equilibrium composition for an initial composition of 4 moles of hydrogen per mole of carbon monoxide and a reactor pressure of 5 atm.

① $\sum \nu_{1j} A_j = 0$

② $\sum \nu_{2j} A_j = 0$

$$\nu = \begin{bmatrix} -1 & -3 & 1 & 1 & 0 \\ -1 & 1 & 0 & -1 & 1 \end{bmatrix} \qquad A = \begin{bmatrix} CO \\ H_2 \\ CH_4 \\ H_2O \\ CO_2 \end{bmatrix}$$

Let us move on to the next problem and the next problem is about calculating the equilibrium equilibrium conversion. So what we have we have been given is in the production of methane from water gas; the following reactions occur namely carbon monoxide plus three moles of hydrogen giving methane and hydrogen and hydrogen plus carbon monoxide giving carbon dioxide plus hydrogen. Calculate the equilibrium constants are given calculate the equilibrium composition for an initial composition of four moles of hydrogen per mole of carbon monoxide and reactor pressure of five atmosphere.

So here what is the knowledge base that we need to use we need to use the condition for equilibrium. There are two reactions so that condition if I write my species as all ages my reaction is summation nu 1 j A j equal to zero and what is my concentration vector; so A 1 A 2 A 3 and so on per this case carbon monoxide, hydrogen, methane, water and carbon dioxide. So I have my four or rather five species two reactions. So this is my first reaction reaction one and reaction reaction two, which is summation nu 2 j A j equal to zero for which I have been given equilibrium constant.

What is my nu matrix stoichiometric coefficient matrix? Again I will not write species on the top and reactions on the side directly write what is it minus 1 minus 3 1 1 0 and then second reaction minus 1 plus 1 then 0 minus 1 again plus 1. The first column belongs to carbon monoxide the second one to hydrogen, third one to methane, fourth one to oxygen and fifth one to carbon dioxide. So given this stoichiometric matrix and my reactions and my equilibrium constant I need to find out equilibrium composition.

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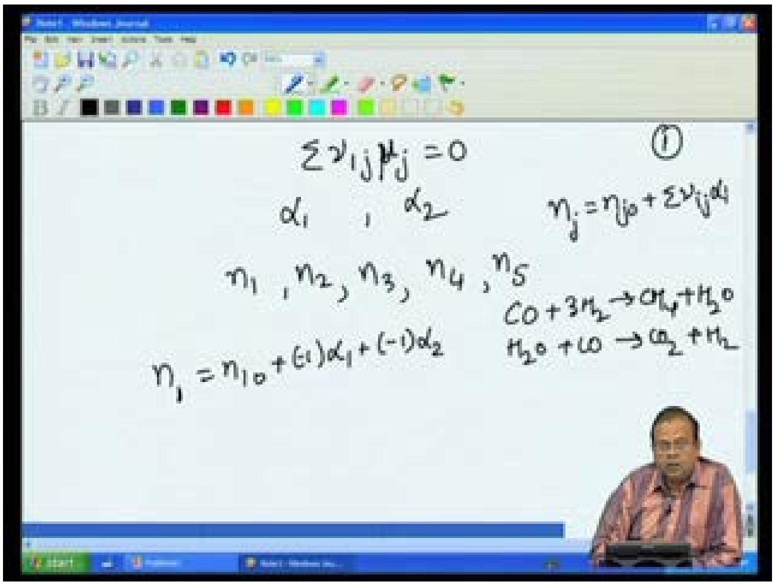

$\Sigma \nu_{1j} \mu_j = 0$

①

$\alpha_1 \quad , \quad \alpha_2$

$n_j = n_{j0} + \Sigma \nu_{ij} \alpha_i$

$n_1 \; , n_2 , n_3 , \; n_4 \; , n_5$

$CO + 3H_2 \rightarrow CH_4 + H_2O$

$H_2O + CO \rightarrow CO_2 + H_2$

$n_1 = n_{10} + (-1)\alpha_1 + (-1)\alpha_2$

So let us try to find out the equilibrium equilibrium composition. So what is it that we are going to use we are going to use the conditions summation nu 1 j mu j chemical potential equal to zero for first reaction same thing for second reaction. There are six species so chemical potentials of the six species; I realize that this is ideal gas. So I can and I can assume perfect mixture and hence use the appropriate equation which I will I will appropriate equation and solve for getting that equilibrium composition. What else do we need to do? We need find is equilibrium composition by finding out to extent can these reactions go.

So let us say that alpha 1 and alpha 2 are are two extent of extent of reactions and we can write number of moles of species one two three four and so on, n 1 n 2 n 3 n 4 n 5 five species. How will we write for example, our first reaction was C O plus 3 H 2 giving CH 4 plus H 2 O and what was our second reaction our second reaction was H 2 O plus CO giving CO 2 plus H 2. So if we take in one that is carbon monoxide it will be n 1 0 plus stoichiometric coefficient in the first reaction times the extent of first reaction. So minus 1 times alpha 1 plus stoichiometric coefficient of second reaction into extent what what is general formula did we did we use. We said that n j is n j 0 plus summation nu i j alpha i.

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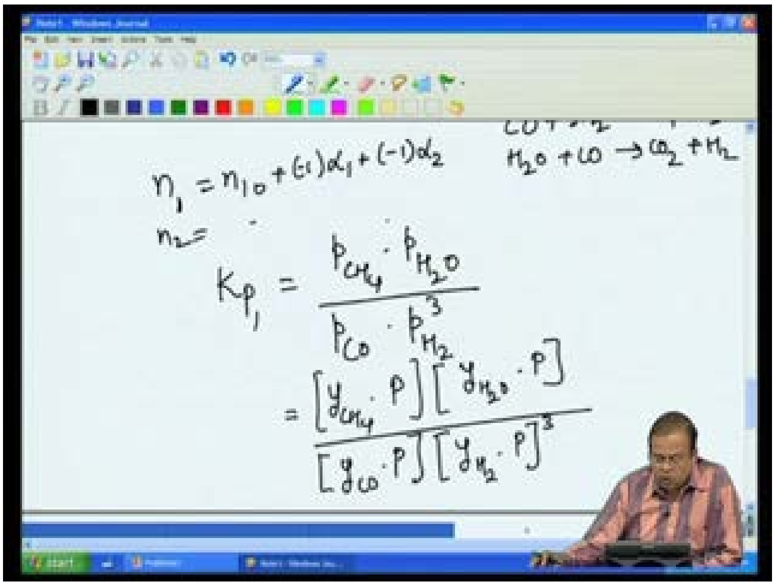

$H_2O + CO \rightarrow CO_2 + H_2$

$n_1 = n_{10} + (-1)\alpha_1 + (-1)\alpha_2$

$n_2 =$

$$K_{p_1} = \frac{p_{CH_4} \cdot p_{H_2O}}{p_{CO} \cdot p_{H_2}^3} = \frac{[y_{CH_4} \cdot P][y_{H_2O} \cdot P]}{[y_{CO} \cdot P][y_{H_2} \cdot P]^3}$$

So if we do for each of these each of these reactions so n 2 n 3 n 4 all the related to alpha 1 and alpha 2. Now we have been given equilibrium constant k p 1 and being being ideal gas perfect gas mixture we can we can write this as partial pressure of methane into partial pressure of water divided by partial pressure of CO into partial pressure of hydrogen res to 3. Where do we get this? We get this from using this thermodynamic equilibrium equilibrium condition.

I can write this in terms of mole fraction of methane into total pressure multiplied by mole fraction of water into total pressure divided by mole fraction of CO into total pressure and similarly, mole fraction of hydrogen into total pressure res to 3 cube root cubes. So what do we get now where do we get mole fractions we are already defined n 1 n 2 n 3 and so on in terms of in terms of this alpha 1 and alpha 2.

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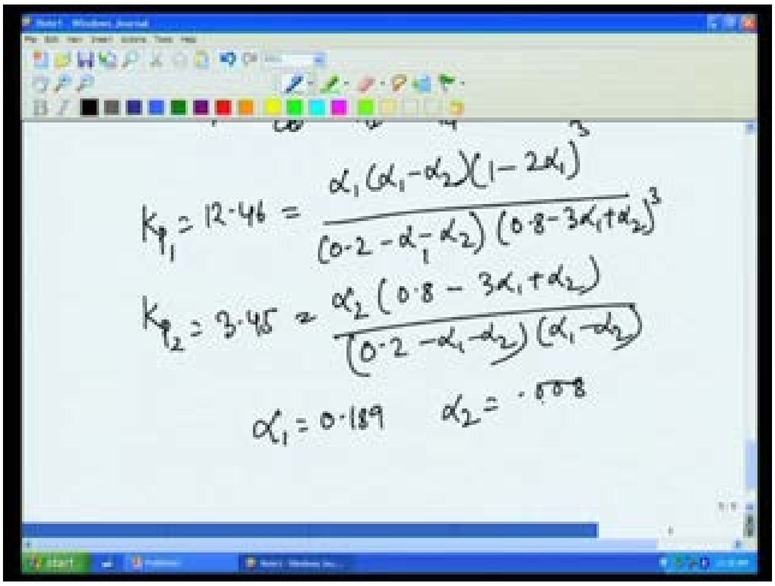

$$K_{p_1} = 12.46 = \frac{\alpha_1(\alpha_1-\alpha_2)(1-2\alpha_1)^3}{(0.2-\alpha_1-\alpha_2)(0.8-3\alpha_1+\alpha_2)^3}$$

$$K_{p_2} = 3.45 = \frac{\alpha_2(0.8-3\alpha_1+\alpha_2)}{(0.2-\alpha_1-\alpha_2)(\alpha_1-\alpha_2)}$$

$$\alpha_1 = 0.189 \quad \alpha_2 = .008$$

We know k p 1 and k p 2 values so I can write the same thing for k p 2 but what will be for example, CH 4 it will be n CH 4 divided by n CH n CO plus n H 2 plus n CH 4 plus n H 2 O; that is number of moles we are getting mole fractions. So if we put all this things toghether we will get one equation if you look at k p 1. So k p 1 which is 12.46 and we put all these information together we will get an equation. Similarly, we will get another equation k p 2 which is 3.45 which again will be in terms of alpha 2 0.8 minus 3 alpha 1 plus alpha 2 divided by 0.2 minus alpha 1 minus alpha 2 into alpha 1 minus alpha 2. So we have two equations two unknowns non-linear equations we can solve them. We get alpha 1 as 0.189 and alpha 2 as 0.008 and from that we can calculate mole fractions.

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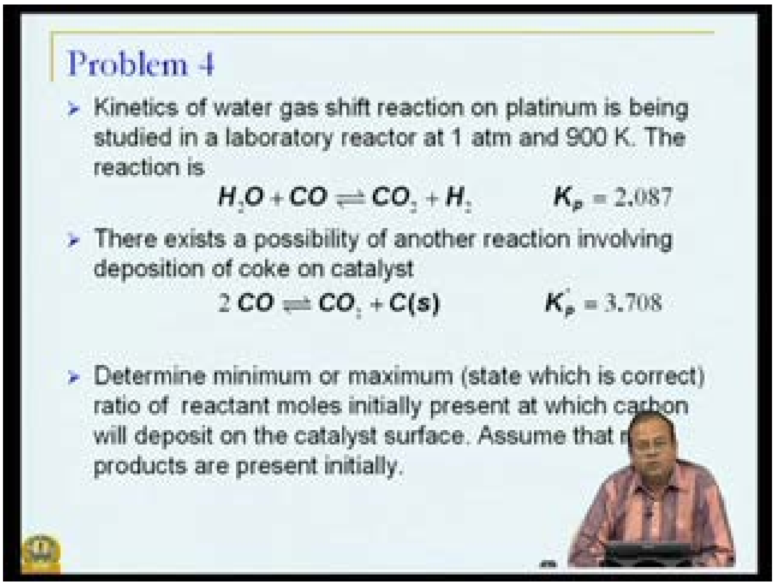

Problem 4

- Kinetics of water gas shift reaction on platinum is being studied in a laboratory reactor at 1 atm and 900 K. The reaction is

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \qquad K_p = 2.087$$

- There exists a possibility of another reaction involving deposition of coke on catalyst

$$2\,CO \rightleftharpoons CO_2 + C(s) \qquad K_p' = 3.708$$

- Determine minimum or maximum (state which is correct) ratio of reactant moles initially present at which carbon will deposit on the catalyst surface. Assume that products are present initially.

Let us look at look at next problem this is that kinetics of water gas shift reaction on platinum is being studied in a laboratory reactor at one atmosphere and 900 k. The reaction is hydrogen plus carbon monoxide carbon dioxide plus hydrogen you have been given equilibrium constant at those conditions. There exists a possibility of another reaction involving deposition of coke on catalyst for which equilibrium constant is also given. Determine either minimum or maximum ratio of reactant moles initially present at which carbon will deposit on the catalyst surface.

Assume that no products are initially present where is a significance of this problem; significance of this problem is that we can there is a possibility that carbon may get deposited on to the on to the catalyst. So we need to conduct these reactions or ensure at at the beginning itself that no carbon gets deposited. So how do we how do we go about solving this particular particular problem.

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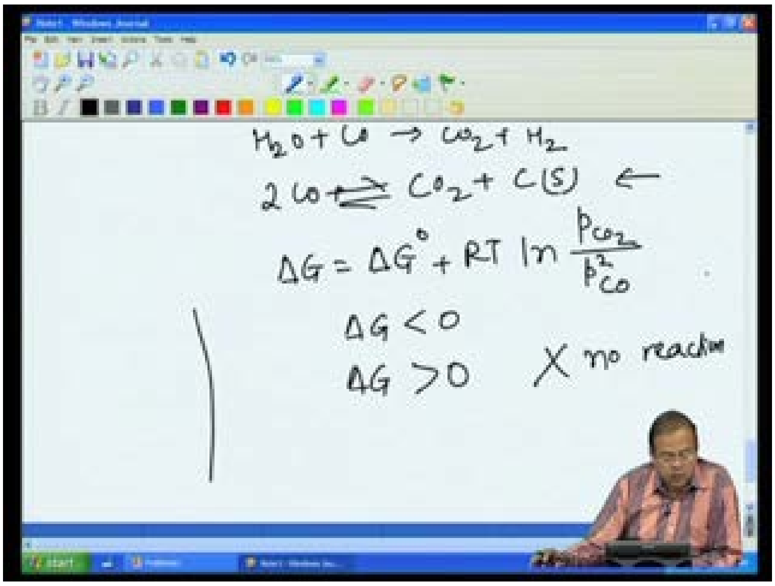

$$H_2O + CO \rightarrow CO_2 + H_2$$

$$2CO \rightleftharpoons CO_2 + C(S) \quad \leftarrow$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_{CO_2}}{p^2_{CO}}$$

$$\Delta G < 0$$

$$\Delta G > 0 \quad \times \text{ no reaction}$$

So what are our reactions? Our reaction is H 2 O plus CO giving CO 2 plus H 2 and what is the second reaction, which we do not want twice CO plus can give rise to CO 2 plus carbon in the solid form. Now we want to avoid this second reaction. So let us focus on focus on second reaction. Now we know free energy change is delta G zero plus RT l n p CO 2 by p square CO. So what is a condition under which reaction will occur reaction will occur if delta G is less than zero other way down reaction would not occur if delta G is greater than zero no reaction.

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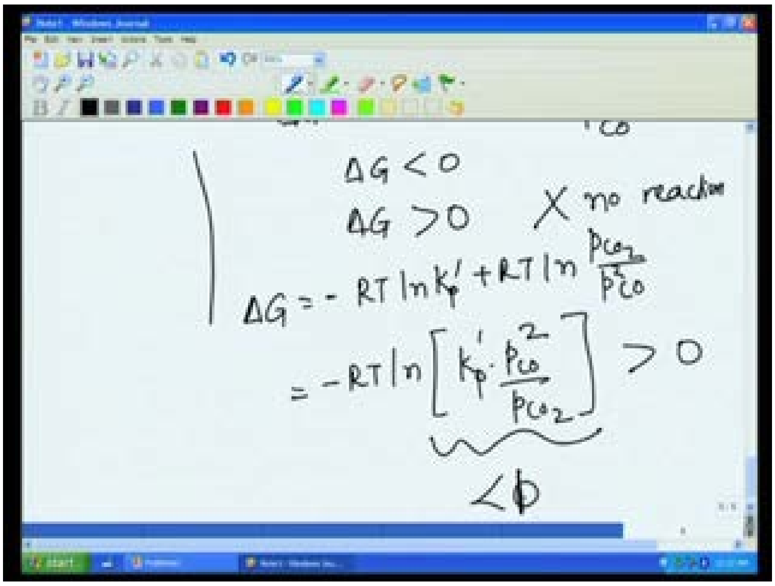

$$\Delta G < 0$$

$$\Delta G > 0 \quad \times \text{ no reaction}$$

$$\Delta G = -RT \ln K_p' + RT \ln \frac{p_{CO_2}}{p^2_{CO}}$$

$$= -RT \ln \underbrace{\left[K_p' \cdot \frac{p^2_{CO}}{p_{CO_2}}\right]}_{<0} > 0$$

So we are looking for this particular particular so we are trying to find out what should be initial pressures initial partial pressures and so on. So I can write now delta G what is my delta G zero is minus RT l n k p prime, why am I using prime because there is a solid phase; so we talked about how we can define the chemical potential and reactions. So that is RT l n p CO 2 by p square CO. Now for this I can further write as this quantity to be greater than zero that means this bracketed quantity has to be less than zero or less than one rather sorry less than one then only delta G zero will be positive.

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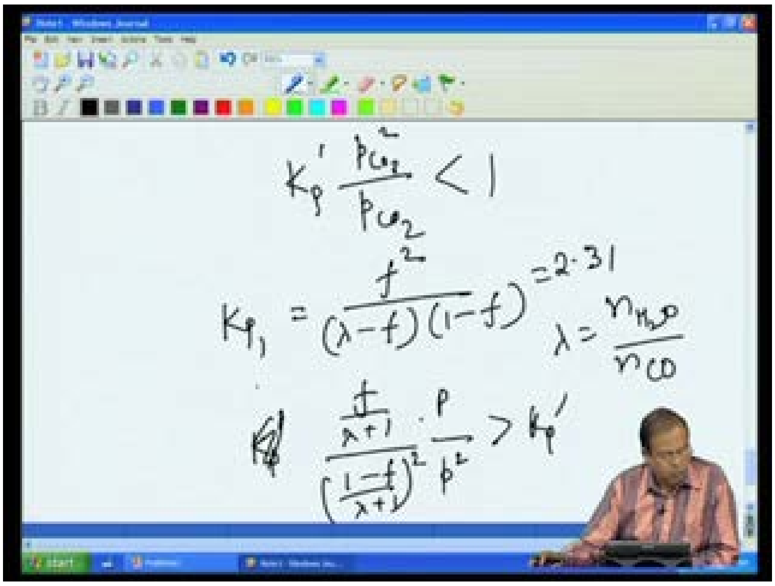

$$K_p' \frac{p_{CO_2}^2}{p_{CO_2}} < 1$$

$$K_{p,1} = \frac{f^2}{(\lambda - f)(1-f)} = 2.31 \qquad \lambda = \frac{n_{H_2O}}{n_{CO}}$$

$$\frac{\frac{f}{\lambda+1} \cdot P}{\left(\frac{1-f}{\lambda+1}\right)^2 P^2} > K_p'$$

So if I now once again once again set up the stoichiometric table and and so on. I want my k p prime into partial pressure of CO square divided by partial pressure of CO 2 to be less than one at the at the at the start up. So I will once again set up the stoichiometric table make use of k p 1 again k p 1 we know what it is. So if we do that we will get in terms of conversion for example, if we define where my alpha 1 my f is conversion and lambda is initial moles of hydrogen to initial moles of carbon monoxide, which is what I want to find out. So this has a value 2.31 and this quantity I need to less than 1. So I have another equation I can write this as so this has to be greater than k p prime.

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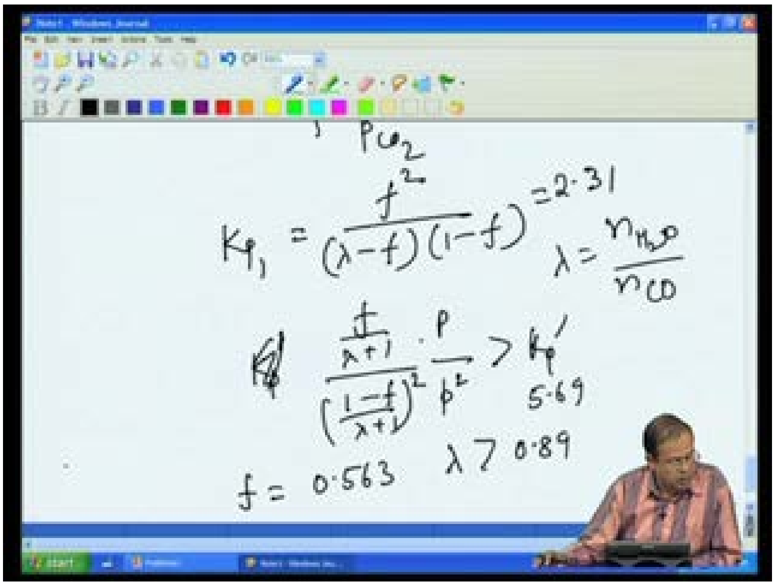

P_{CO_2}

$$K_{p_1} = \frac{f^2}{(\lambda - f)(1-f)} = 2.31 \qquad \lambda = \frac{n_{H_2O}}{n_{CO}}$$

$$\frac{\frac{f}{\lambda+1}}{\left(\frac{1-f}{\lambda+1}\right)^2} \cdot \frac{P}{P^2} > K_p' \quad 5.69$$

$$f = 0.563 \qquad \lambda > 0.89$$

So if I now solve this two for for that is I know one relationship between f and lambda I know another relationship this value is given as 5.69. So first I can solve it using equal to and then if I do that I get f equal to 0.563 and lambda equal to 0.89. So if my lambda is greater that means initial moles of water to carbon monoxide is greater than 0.89. I will not have this reaction or carbon deposition will not take place so various different ways in thermodynamics can be useful.

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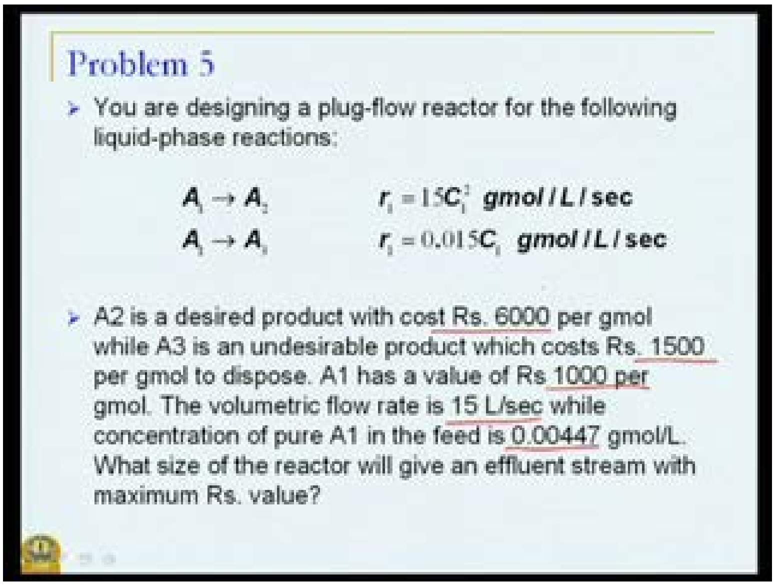

Problem 5

- You are designing a plug-flow reactor for the following liquid-phase reactions:

$$A_1 \rightarrow A_2 \qquad r_1 = 15C_1^2 \ \ gmol/L/sec$$
$$A_1 \rightarrow A_3 \qquad r_2 = 0.015C_1 \ \ gmol/L/sec$$

- A2 is a desired product with cost Rs. 6000 per gmol while A3 is an undesirable product which costs Rs. 1500 per gmol to dispose. A1 has a value of Rs 1000 per gmol. The volumetric flow rate is 15 L/sec while concentration of pure A1 in the feed is 0.00447 gmol/L. What size of the reactor will give an effluent stream with maximum Rs. value?

Let us look at the next problem. You have a plug flow reactor for two reactions A 1 going to A 2 and A 1 going to going to A 3 the kinetics is given. We know it too is a desired product, which cost a rather which can bring us 6000 rupees per gram mole; A 3 is undesirable which cost 1500 to disposed. So not only it is undesirable but it cost money to get rid of it and A 1 has a value of 1000 rupees per gram mole volumetric flow rate is fifteen litres per second, while concentration of pure A 1 in the feed is also given.

What size reactor will give an effluent stream with maximum maximum value? How do we how do we solve this. Now what will be the maximum value what will be the value of the product stream value of the product stream will be the value because we can sell A 2 minus the cost, which is required to dispose A 3 and minus the raw material cost.

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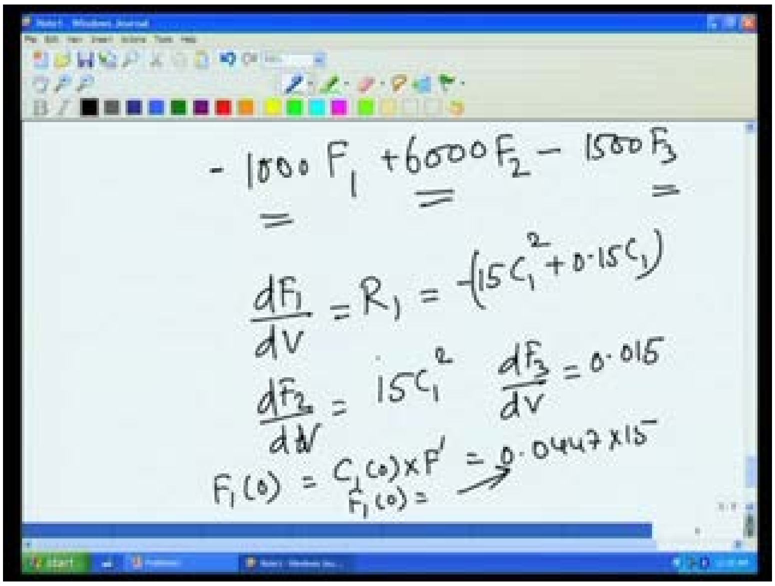

$$\underline{\underline{-1000\,F_1}} + 6000\,\underline{\underline{F_2}} - 1500\,\underline{\underline{F_3}}$$

$$\frac{dF_1}{dV} = R_1 = -(15C_1^2 + 0\cdot15C_1)$$

$$\frac{dF_2}{dV} = 15C_1^2 \qquad \frac{dF_3}{dV} = 0\cdot015$$

$$F_1(0) = C_1(0) \times F' = 0\cdot0447 \times 15$$

$$F_1(0) = \nearrow$$

So if I want to solve this problem first of all I would need to find out this value. What value would we need to find out? We need to find out 1000 let us say molar flow rate of species one is f one that is a price I will fetch by selling selling my desired product it to or or i should minus 1000 it is cost plus 6000 into F 2 minus 1500 into F 3 I want to dispose of which cost money that is this raw material cost and the selling price of my desired product. How do we do this we have dF 1 dV which is R 1 net rate of conversion of conversion of species, which in this particular case if we take the corresponding rates of two reactions R 1 and R 2 we can write this as 15 C 1 square plus 0.15 C 1, dF 2 dV as 15 C 1 square.

So we are just writing the mole balances for three species mole balances for three species. What else is given to us it says that the volumetric flow rate is known and a concentration in the feed is known. So what is my F 1 in the feed is concentration in the feed multiplied by my volumetric flow rate and there are no products in the feed. So I know what is that is 0.00 so I know what is my F 1 0 this value, F 2 0 F 3 0 all zero no no products in the in the feed. So I can solve this three differential equations one two three with the initial condition that F 1 at v equal to zero is this particular value. And then look at how this function behaves and wherever we get zero maximum value that is the volume that we should be using. And it turns out for this particular problem that volume if you try to solve this equations is 896 litres.

So these are the few examples that we may encounter, there are many more but our time is time is limited, if you open any standard reaction engineering book, you will find problems of this nature and many more, but my point in solving this problems is just to give you a head start. Thank you.