Advanced Chemical Reaction Engineering
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Lecture - 6
Illustrative Examples
(1) Plug Flow Recycle
(2)Multiple Reactions-I

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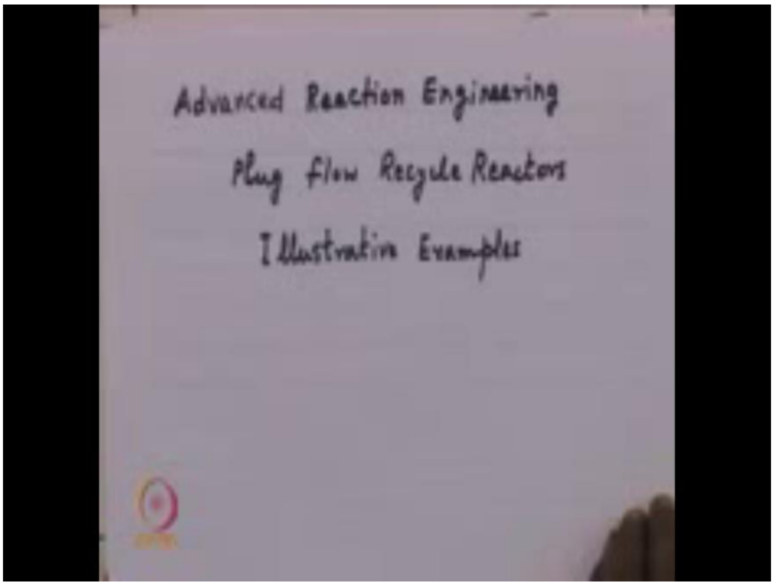

Advanced Reaction Engineering

Plug flow Recycle Reactors

Illustrative Examples

Go we gets started with plug flow recycle reactors. Today, I look at some illustrative examples just to say how this system will behave.

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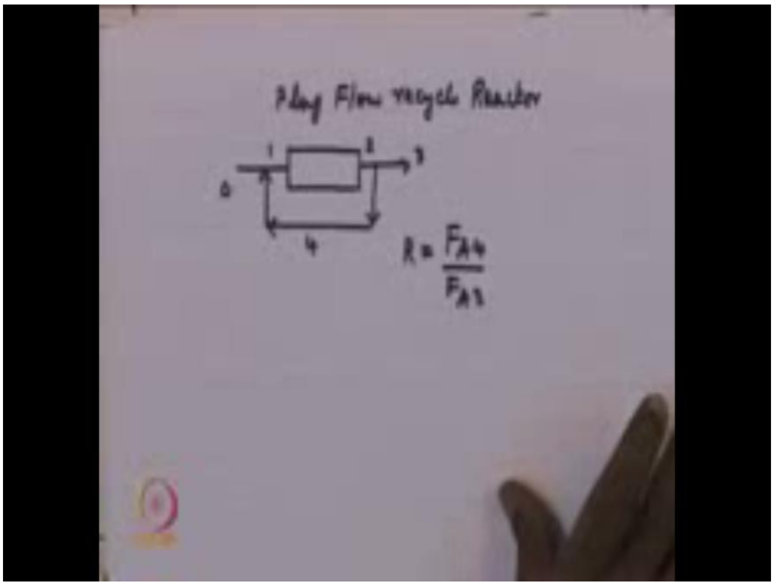

Plug Flow recycle Reactor

$R = \frac{F_{A4}}{F_{A3}}$

So, our system we have set earlier looks like this. You have a plug flow vessel here it may contain a catalyst or it may have in inert for through which you have reactance of flowing. And there is the recycle that recycle ratio is defined as F A 4 divided by F A 3.

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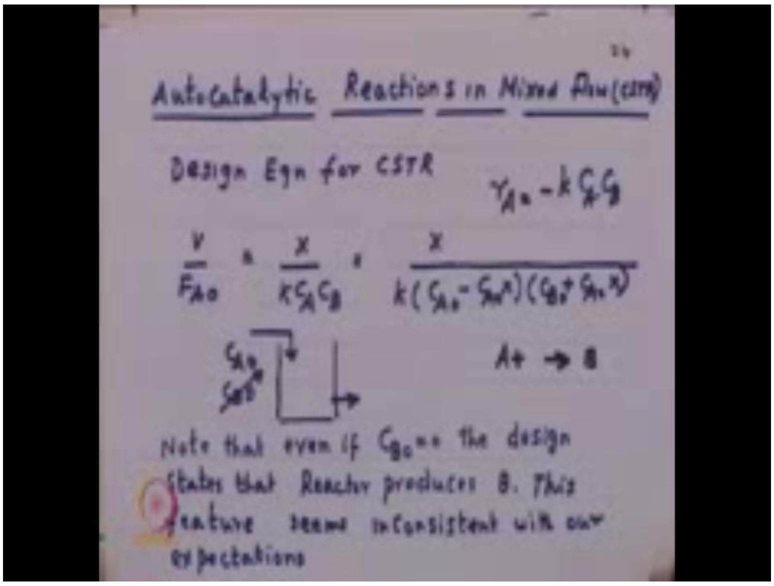

Autocatalytic Reactions in Mixed Flow (CSTR)

Design Eqn for CSTR

$r_A = -k C_A C_B$

$\frac{V}{F_{A0}} = \frac{X}{k C_A C_B} = \frac{X}{k(C_{A0} - C_{A0}X)(C_{B0} + C_{A0}X)}$

A+ → B

Note that even if $C_{B0} = 0$ the design states that Reactor produces B. This feature seems inconsistent with our expectations

This is r recycle ratio. An example that of importance to us is use of auto catalytic reactions in mixed flow. Because mixed flow is a form in which this context becomes so what I have got here is there it design equation for as CSTR where the reaction is occurring where the rate function is given by C A C B and the reaction is A its auto catalytic so A giving B. But its auto catalytic therefore, it depends on both A and B. Now, point that I had want to get a cross to you is that when you look at this equation you find that even C B 0 is 0 this size of the equipment is finite .The reasons is not obvious from here y z that even though you do not put C B 0 in the field that the reactor gives you a finite the result. Because you would expect that there should be C B 0 in the field. Now, we explain this so just explain this once again just to put it in the context.

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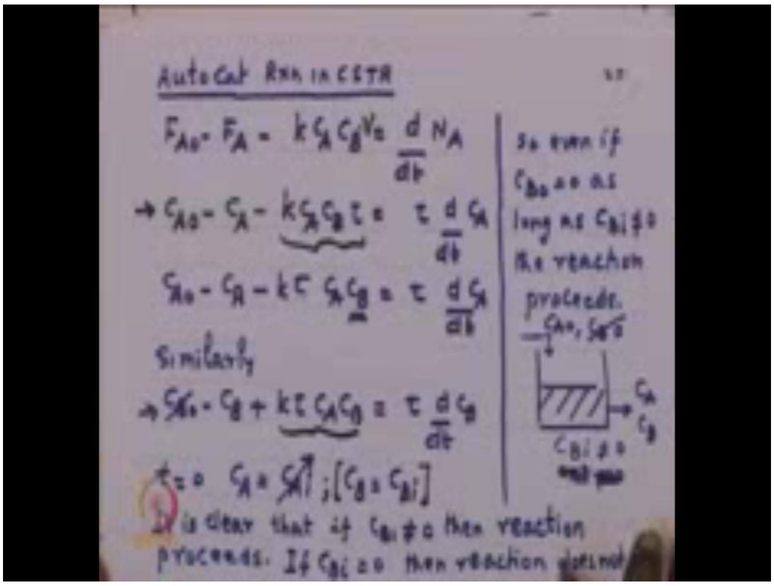

AutoCat Rxn in CSTR

$F_{A0} - F_A - k C_A C_B V = \frac{dN_A}{dt}$

$\rightarrow C_{A0} - C_A - \underbrace{k C_A C_B \tau} = \tau \frac{dC_A}{dt}$

$C_{A0} - C_A - k\tau C_A C_B = \tau \frac{dC_A}{dt}$

Similarly

$\rightarrow C_{B0} - C_B + \underbrace{k\tau C_A C_B} = \tau \frac{dC_B}{dt}$

$t = 0 \quad C_A = C_{Ai} \, ; [C_B = C_{Bi}]$

It is clear that if $C_{Bi} \neq 0$ then reaction proceeds. If $C_{Bi} = 0$ then reaction does not

So even if $C_{B0} = 0$ as long as $C_{Bi} \neq 0$ the reaction proceeds.

To understand this, what we said is that let us look at the unsteady state when you look at the unsteady state what we have a material balance for A your material balance for B. And this term which represents the reaction rate function when you put C A i as 0 and C B i as finite what we said is that as long as C A i, because C A is coming in therefore, the reaction rate is 0 at 0 times. But as time proceeds since C A coming in this function becomes finite. As it result what happens is that at steady state there is the effect of C B which is there when you started of the equipment. So, what we trying to say is that as long as material is there when you start the equipment CSTR will always give you a finite result. So, that is on other words what we saying is CSTR is an instance of infinite amount of recycle. Therefore, the material that if started at some time in the pass history always linkers there how are, small in may be that is the point that we must remember. Now, suppose we look at the other example which is a PFR.

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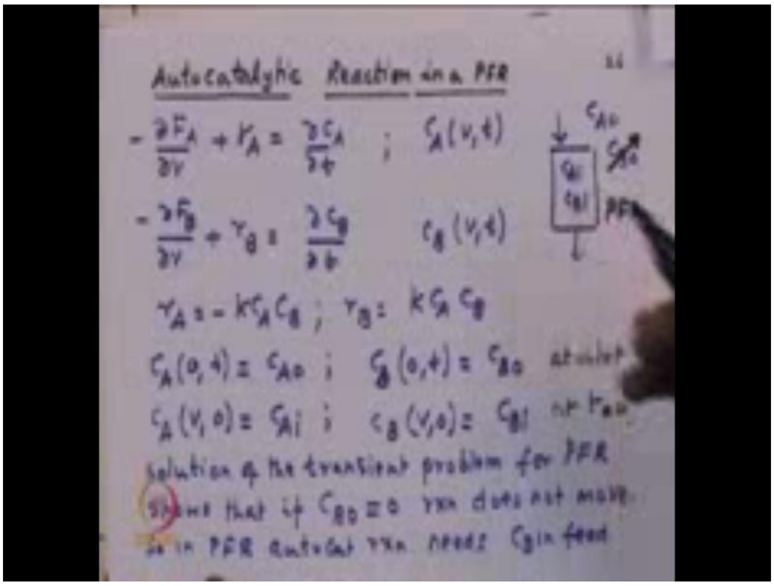

Autocatalytic Reaction in a PFR

$-\frac{\partial F_A}{\partial V} + r_A = \frac{\partial C_A}{\partial t}$; $C_A(V,t)$

$-\frac{\partial F_B}{\partial V} + r_B = \frac{\partial C_B}{\partial t}$ $C_B(V,t)$

$r_A = -kC_AC_B$; $r_B = kC_AC_B$

$C_A(0,t) = C_{A0}$; $C_B(0,t) = C_{B0}$ at inlet

$C_A(V,0) = C_{Ai}$; $C_B(V,0) = C_{Bi}$ at t=0

Solution of the transient problem for PFR

Show that if $C_{B0} = 0$ rxn does not move

in PFR autocat rxn needs C_B in feed

For example, there is no recycle where you have material coming in material going out its a PFR which means the recycle ratio is 0. And it has initially let us says certain amount of C A i certain amount of C B i as an example. Let us see what happens? So, I have just written the unsteady state the equation for have PFR we were del F del v is volume reaction rate and this the accumulation term I have written for term for both component a and component b. Now, if it look at the what have what is happening to C A at 0 0 means at inlet at any time it is see that means what is coming in C A 0 similarly, what is coming in C B 0?

And it any position inside at 0 time I have taken C A i and C B i and other words what we have saying in that we have plug flow vessel which initially contain C A i C B i to which you start which C A 0 and C B 0 what happens to this process? What I am trying to say that if C B 0 is 0 if C B 0 is 0 what will happen is that the reaction will proceed as long as there is some C B i. But this C B i will get knock out after sometime and moment C B i gets knock out there is now further C B inside the process. And therefore, this rater function term will always be 0 and therefore, auto catalytic reaction in a PFR will not take off. Because there is no C B whatever C B was there as been knock out and has soon as C B is knock out that reaction stops. So, in a CSTR auto catalytic reaction always goes forward wait in the case of a PFR auto catalytic reaction does not move, because there is no product.

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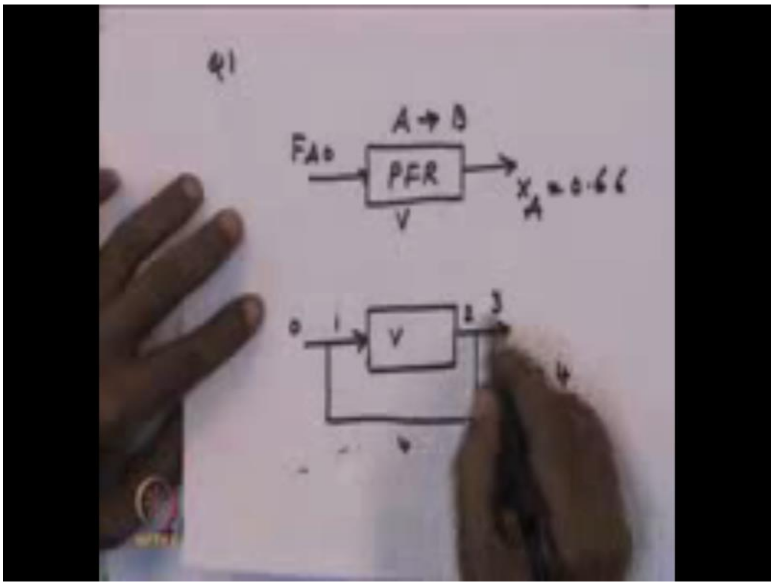

With this let as quickly look at 1 or 2 small examples to understand how was how the numbers look like? See after all find its numbers that matter this small exercise what I have got here is that you have given data there is some data which is given. It’s says there is the PFR in which this reaction A goes to B is taking place and experimentally you find out that it gives you a conversion of 0.66. It is an experiment you have done and you find that the conversion is 0.66. Now, you put a recycle pump and put it back that means the same reactor of volume v is also same volume v. Now, it is there is the recycle the recycle ratio is given as 4 what is the likely extent of reaction likely conversion you will expect. Now, of course, we know that when you recycle your conversion offers, because the fact that you know it is a measure of mixing so how do you find out? To find out which we recognize something that we said little earlier and the earlier classes.

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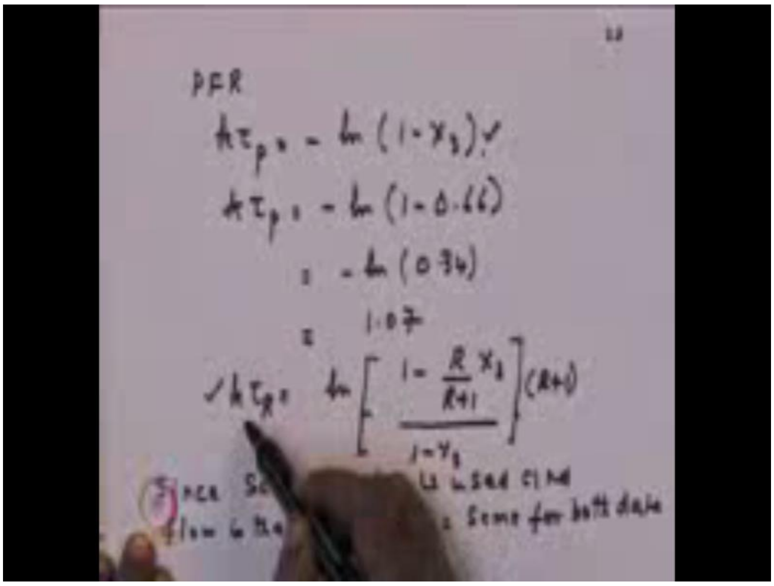

PFR

$k\tau_p = -\ln(1-x_3)$ ✓

$k\tau_p = -\ln(1-0.66)$

$= -\ln(0.34)$

$= 1.07$

✓ $k\tau_R = \ln\left[\frac{1-\frac{R}{R+1}x_3}{1-x_3}\right](R+1)$

Since Sa … is used since

flow is the … = Same for both data

For that if you have a plug flow device there it relationship between k tau p and x 3 x 3 by x 3 I mean what x 3 is this at the end of the reactor. So, this we have derived already and similarly, if it is a recycle reactor then this is the kind of relationship between residence time rate constant and recycle ratio these also we have done earlier. So, what are we saying now? The same reactor you are using with the recycle of 4 which means what? Tau p equal to tau r same reactor you are using as the recycle tau p equal to tau r. So, what it means that in this exercise x a is given as 0.66 which means if you put x a same as the x 3 is 0.66 you can find out k tau p which if you plug in here you be able to find out the conversion you understand. That means essentially the data for a PFR is given x 3 is given so you know k tau p since same reactor is used k tau r is specified therefore, you can find out the A conversion.

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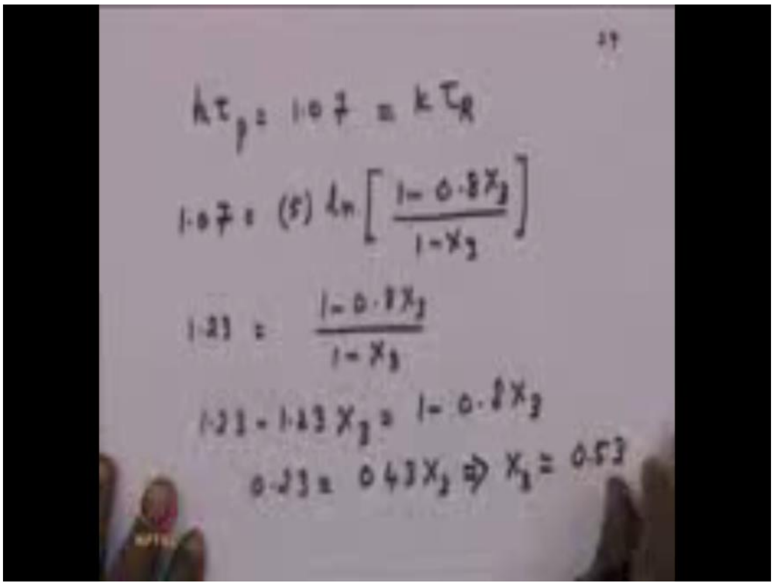

$k\tau_p = 1.07 = k\tau_R$

$1.07 = (5)\ln\left[\frac{1-0.8X_3}{1-X_3}\right]$

$1.23 = \frac{1-0.8X_3}{1-X_3}$

$1.23 - 1.23X_3 = 1-0.8X_3$

$0.23 = 0.43X_3 \Rightarrow X_3 = 0.53$

So, I have done this calculation and the answers you get is not 0.66, but is lower is what is the expected. So, what is the message that we want to take from here is that when you recycle you will find that you will lose some amount of conversion. Because the recycle actually is form of mixing and mixing reduces the extend of reaction. So, it is another example which we have taken here this I want to spend some time on this.

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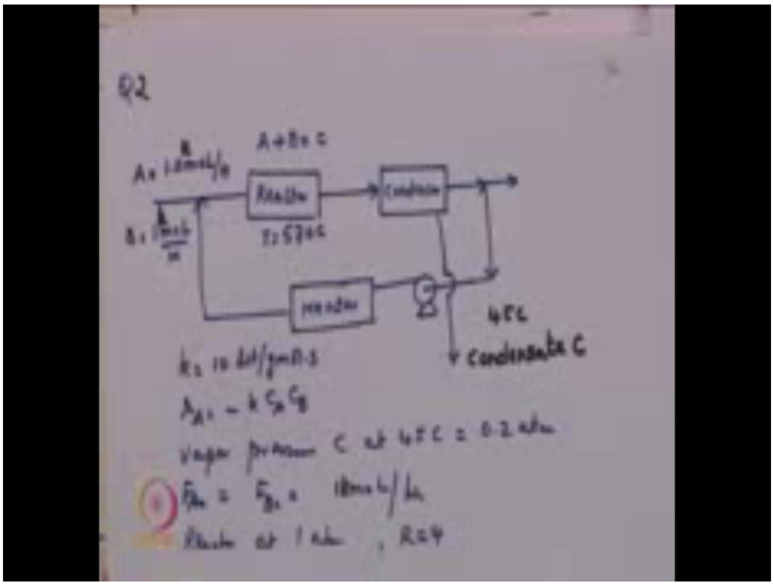

$k = 10$ lit/gmol.s

$-r_A = kC_AC_B$

Vapor pressure C at 45 C = 0.2 atm

$F_{A0} = F_{B0} = 10$ mol/hr

Reactor at 1 atm , R=4

What I got here you have a reactor it is operating at 570 C most of this data is taken from an industry and it goes to condenser. The reaction is A plus B going to C and then it goes to condenser where the condensable gas C is the condensable gas which condenses so this is condensate. Now, you are putting the recycle after the condensate you putting a recycle and then you heat it up. Because the reactor is 570 that condensate this condensed the operating a 45c the data is given. Therefore, you have to reheated and put in back in to the equipment. Now, this is a fairly common kind of device you will see in the process illustrate. That there is the reactor and the reaction does not go to completion you try to recover whatever is useful to you and whatever is not useful to you put in back to the process something that we will do any way. So, data given is that the rate constant is given by looking at the form of rate function rate constant it is the second order reaction. So, it is k times C A C B is rate function so rate function is k times C A C B. And this is 1 kilo mole per hour and this made a mistake 1 kilo mole per hour please make that correction not 1.

But 1 mole kilo per hour vapor pressure of C is given as 0.2 atmosphere and moles of A and B are equal so we 1 kilo mole per hour 1 kilo mole per hour reactors at 1 atmosphere recycle ratio is 4 this all is given. Because of this condensation what is the effect you anticipate in the process? Suppose this condenser was not there are the condenser was there it is in irreversible reaction I am not saying its reversible reaction. It is irreversible reaction what is the effect that you would anticipate is product will go back, but this not a reversible reaction. This the reaction is not reversible see it rate functions says k times C A C B therefore, even if there is C present here it does not affect the reaction. At least this how it is formulated so the way it is formulated it appears that it does not the affect. I am at write would that make sense to you to what effect do we anticipate? To the extended the C is occupying part of the gas phase the reaction what this is now, let us to understand this. Just to understand this I have done a small calculation I want it to appreciate this what I have done is have written the stichometry.

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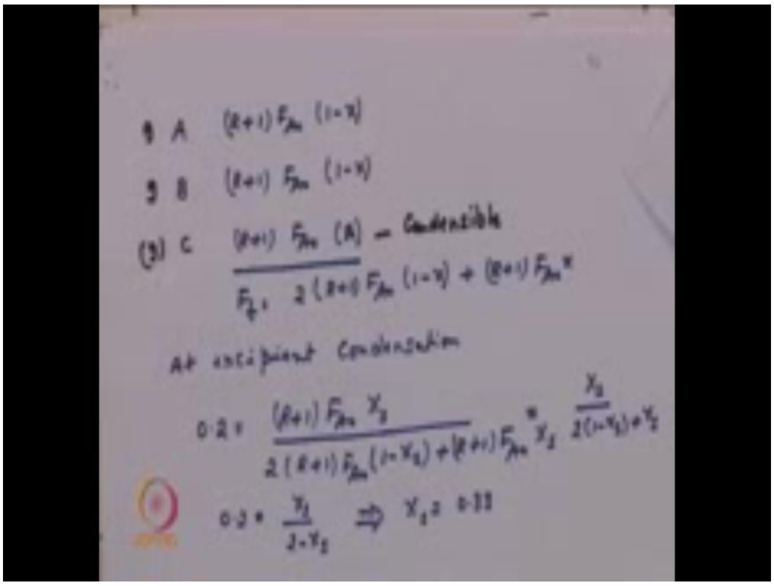

1 A $(R+1)F_{A0}(1-x)$

1 B $(R+1)F_{A0}(1-x)$

(1) C $(R+1)F_{A0}(x)$ – Condensible

$$F_T = 2(R+1)F_{A0}(1-x) + (R+1)F_{A0}x$$

At incipient condensation

$$0.2 = \frac{(R+1)F_{A0}x_1}{2(R+1)F_{A0}(1-x_1)+(R+1)F_{A0}x_1} = \frac{x_1}{2(1-x_1)+x_1}$$

$$0.2 = \frac{x_1}{2-x_1} \Rightarrow x_1 = 0.33$$

This is the stichometry A and B are going in there all gases A is the gas B is the gas and C is the condensable gas it is a condensable gas. Now, what is the total moles adjust add in small up this is the total moles R plus 1 F A 0 this is our conversion. Our conversion is that inside the recycle loop we take R plus 1 F A 0 also our basis R plus 1 x R plus 1 in and then the product is R plus 1 F A 0 x. So, what I have done is at the incipient condensation what is meant by insipient condensation when the gas phase is saturated which C. So, at the insipient condensation is in pressures 1 atmosphere the mole fraction of component C in the gas phase must be given by this relationship amount of C divided by that total mole yes or no?

So, if you solve this you find that excess 0.33 what are we saying? At incipient condensation the gas phase should the excess is 0.33 what is it mean? Now, what we are saying is till x becomes 0.6 0.33 there is no condensate till x becomes 0.33 there is no condensate. You condenser has no it does not any performing function, because still the gas is saturated only after the gas is saturated little start condensing. So, this effect that x equal to 0.33 and therefore, to that that gas phase after see saturation only it starts condensing will affect the gas flow that goes back to the reactor how do we take that into account?

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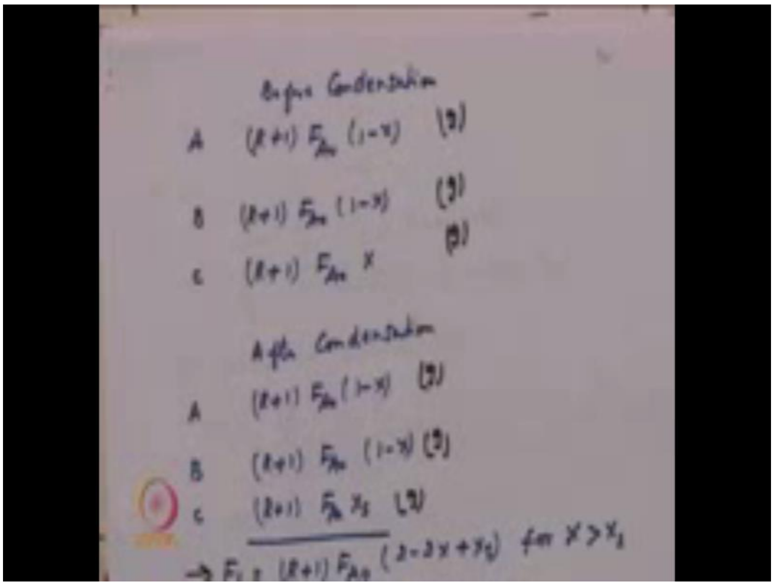

Before Condensation

A $(R+1) F_{A0} (1-x)$ (g)

B $(R+1) F_{A0} (1-x)$ (g)

C $(R+1) F_{A0}\, x$ (g)

After Condensation

A $(R+1) F_{A0} (1-x)$ (g)

B $(R+1) F_{A0} (1-x)$ (g)

C $(R+1) F_{A0}\, x_s$ (g)

$\rightarrow F_t = (R+1) F_{A0} (2-2x+x_s)$ for $x > x_s$

Take their into account what I have done is before condensation what was the stichometry after condensation what is the stichometry? Before the conversation is what everything is in the gas phase everything in the gas phase and after though after is started to condense what will happen? The gas phase will have the excess this amount of the amount of see in the gas phase is given by this relationship excess of that will condense in the gas phase the so much material will be there in excess of that will be condensed. Therefore, what we will find is that moles of F t that you will see going through the equipment is given by this is the correct what I am saying F t R plus 1 F A 0 2 minus 2 x plus x s this is what goes through the equipment, is it alright.

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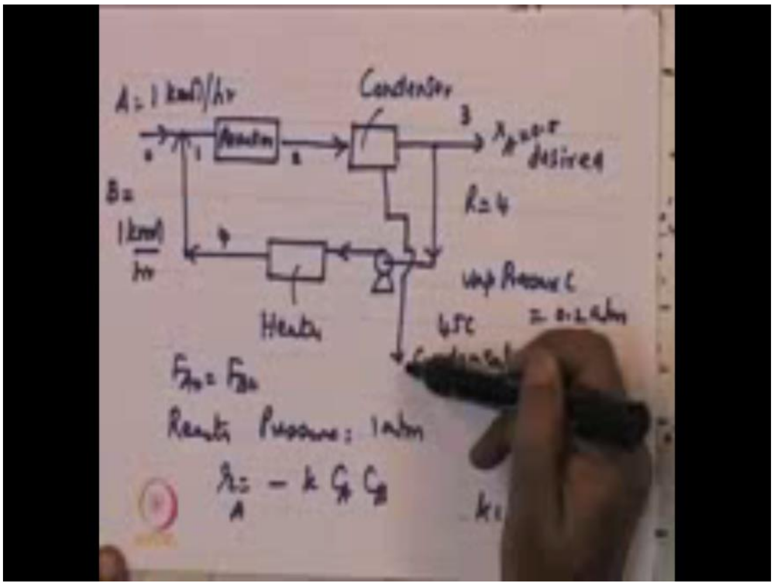

Now, notice what we have been trying to do? What we have been trying to do this exercise is trying to set up a procedure for doing reactant design calculation for this situation while there is the condenser where there is the condensate is take place. And what we want to draw your attention is that incase on the situations like this you must first calculate what is the a conditions and which the condensation begins? So that we can take in appropriate decision regarding how to do the calculation this is the exercise let we are trying to do.

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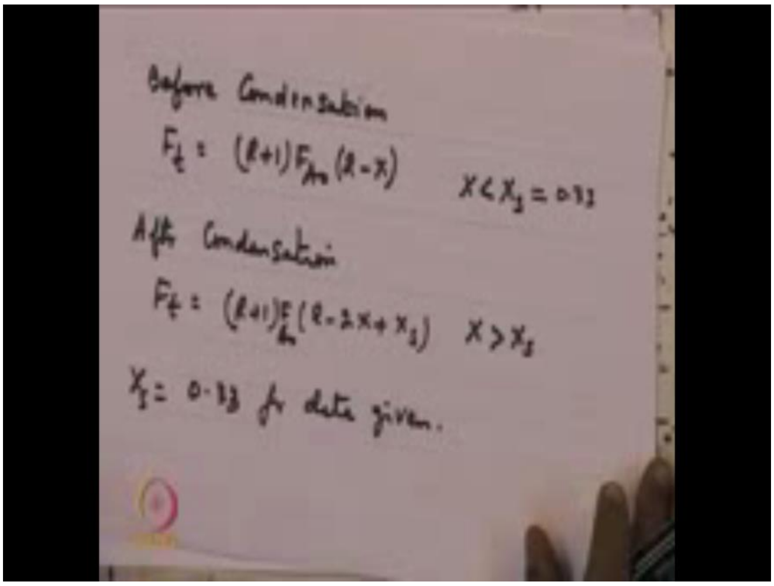

Before Condensation

$F_t = (R+1)F_{A0}(2-X)$ $\quad X < X_3 = 0.33$

After Condensation

$F_t = (R+1)F_{A0}(2-2X+X_3)$ $\quad X > X_3$

$X_3 = 0.33$ for data given.

So, let us recognize that before condensation before condensation that the total mole of flow at the reactor exit is given by R plus 1 F A 0 2 minus of x this for x less than x s and we shown that x s equal to 0.33 we already shown that. Now, after condensation you find x s is F t is R plus 1 F A 0 2 minus of 2 x plus x s this is the after condensation where x s is 0.33 moment we recognize this all the rest becomes fairly straight forward.

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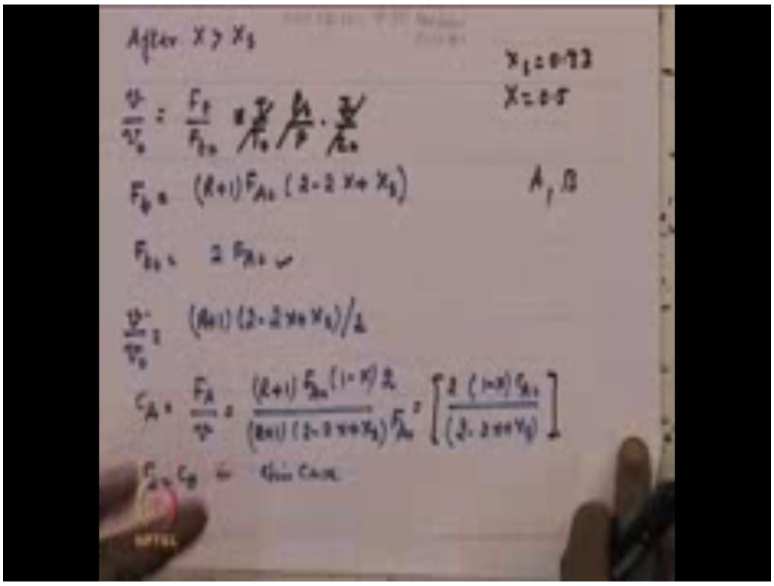

After $x > x_s$

$x_s = 0.33$

$x = 0.5$

$\frac{v}{v_0} = \frac{F_t}{F_{t0}} \cancel{\frac{T}{T_0}} \cancel{\frac{P_0}{P}} \cdot \cancel{\frac{Z}{Z_0}}$

$F_t = (R+1)F_{A0}(2-2x+x_s)$

A, B

$F_{t0} = 2F_{A0}$ ✓

$\frac{v}{v_0} = (R+1)(2-2x+x_s)/2$

$C_A = \frac{F_A}{v} = \frac{(R+1)F_{A0}(1-x)2}{(R+1)(2-2x+x_s)F_{A0}} = \left[\frac{2(1-x)C_{A0}}{(2-2x+x_s)}\right]$

$C_A = C_B$ ← this case

Now, what is volumetric flow v by v 0 after x x greater than x. Because our interest is x equal to 0.5 and x s a being equal to 0.33 our interest is x greater than x. So, we know what is v by v not from our gas law we know it is F t by F t 0, T by T 0, P 0 by P, Z by Z 0 if it is an ideal gas we know that this is 1; this is 1; this is 1. Therefore, F t becomes a F A 0 r plus 1 F A 0 2 minus of 2 x plus x s. And F t 0 we already given that it is a mole equal mole of flow of A and B where a is and therefore, it is 2 F A 0.

Therefore, v by v 0 is simply v by v 0 F t by F t 0 we can put this as equal to what is already mention the R plus 1 2 minus 2 x plus x 2 what is C A? By definition F A by v, therefore you can substitute for F A which is F R plus 1 F A 0 1 minus of x and what is v? We have already calculated v 0 times is whole thing what is v 0? v 0 v by v 0 is the that is the effort we are substitute for v is v 0 times is whole thing that is why we get this fairly simplified expression. So, what we have trying doing here is that after all any rate expression requires concentration in terms of conversion. And therefore, we have derived concentration in terms of conversion we are now, therefore, in at position to substitute our rate function in terms of conversion we can integrate find the reactive volume.

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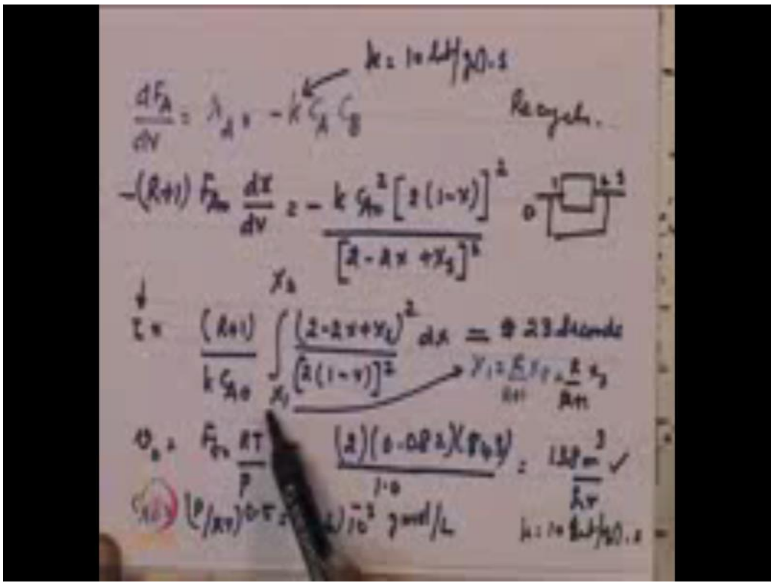

So, what is the reactive volume? The reactive volume if we want to calculate for a recycle reactor we said d F by d v is r A r A is k C A C B and we know what is C A and what is C B just now. We can substitute for all that and therefore, we get an expression for the residence time in a recycle reactor in terms of all these variables. We can simply this in show that residence time in simply R plus 1 by k C A 0 integral x 1 to x 2 of all this expressions. Notice here, that x 1 C our recycle reactor looks like this where this is 0, this is 1, this is 2 and this is 3. And we should shown already that x 1 x 1 is R by R plus 1 x 2 same as R by R plus 1 x 2 we know we will shown on all that.

Therefore, we can do this integration I have put in all the numbers v 0 is what in this particular 2 kilo miles per hour and so on. I will calculate the mole of flow rate as so many cubic meters per hour and concentration at the reactor in let C A 0 v by R T that comes out to be a 3.6 10 minus 3 gram moles per liter. So, we know C A 0 and k value is given as 10 liters per gram mole per second I will write here k equal to 10 liter per gram mole per second. So, k is also given we can calculate all this numbers and that is how I got this numbers as 23 second when k is equal to 10 liter on per second.

So, what I have we done? What we have done is that for a recycle reactor we have put setup the rate expression and then we substitute for C A and C B and then the replace is

F A as R plus 1 F A 0 1 minus of x and that is how we got the residence time. By this expression you have done this integration and found out the residence time 23 second. By the x 1 the lower limit is taken is R by R plus 1 x x 3 same at R by R plus 1 x 2 by R value is given as R equal to 4 is given at the problem statement. Now, that we have that done the residence time what is the reactor volume?

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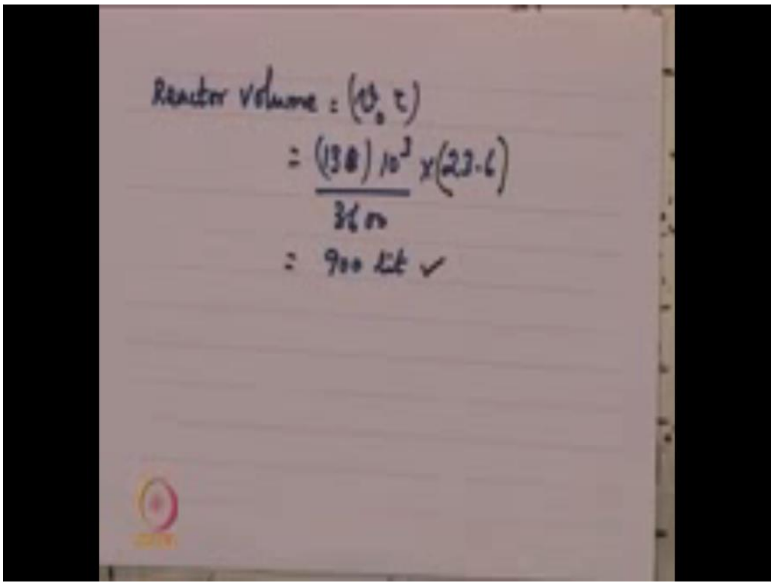

Reactor volume $= (v_0 \tau)$

$$= \frac{(138)\,10^3}{3600} \times (23.6)$$

$= 900$ lit ✓

Reactor volume is simply given as reactive volume is simply given as a volumetric flow multiplied by there is residence time what is the volumetric flow? It is 138 cubic meters per hour at divided by 3600 seconds cubic meters I will convert to liters. And then so many seconds so you get 900 liter per for the processing of 1 kilo mole per hour. So, what we have trying to say here is that it just quickly recalls what are we trying to do? What we have try to do is we have A going in at 1 kilo mole per hour B going in at 1 kilo mole per hour into the reactor why the second order reaction r A equal to k C A C B is taking recycle ratio is R. And we want x A equal to 0.5 since this is component A plus B equal to C I have write here A plus B equal to C. And since C is the condensable gas you will find that this exit here moment after condensation you will find that this gas always saturated this. So, that effect is this entire take into account so that we do the calculation as for procedure. This what we are trying to do and for the case of k equal to 10 liters per gram mole per second we find for 1 kilo mole per hour of flow we find that we required the volume of 900 liters.

So, in the recycle plug flow what we have trying to demonstrate is that we basis that we have to choose is R plus 1 F A 0 number 1. Second point that we have trying to say is that, because of recycle the there is mixing inside the equipment therefore, you will lose on conversion. And therefore, you can use the recycle reactor device as the way of understanding what is the extends of mixing that takes place the equipment? That thing we said if it is in auto catalytic reaction the recycles are required otherwise the reaction does not go forward. But the fact that you know there is recycle and therefore, the reaction goes forward. If it is infinite recycle like that of a stead tank it made appear that you have not a put any recycle in the feed. But actually, because of the fact that the so much of recycle internally you do not have to put it continuously these are the points that we have made in our presentation.

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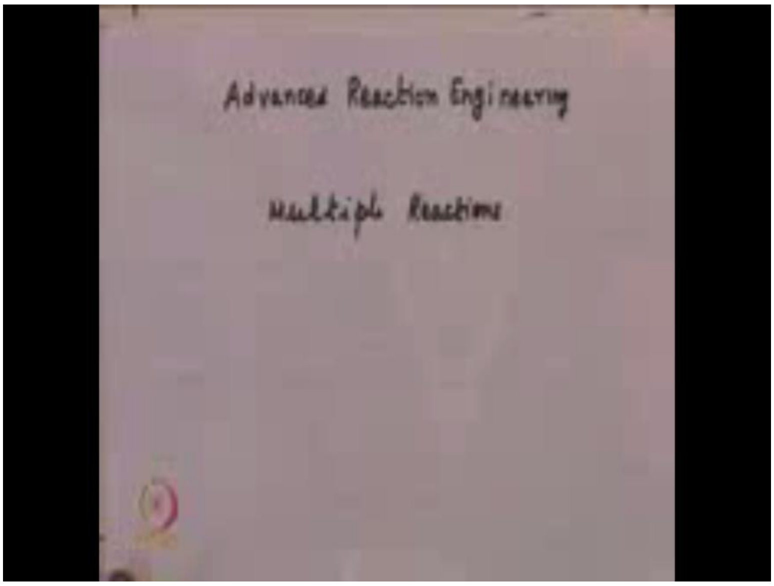

Advanced Reaction Engineering

multiple Reactions

So, now this we will go on to our next topic by which we want to do this multiple reactions. So, we have been writing our stichometry for single reactions so we want to write are stichometry.

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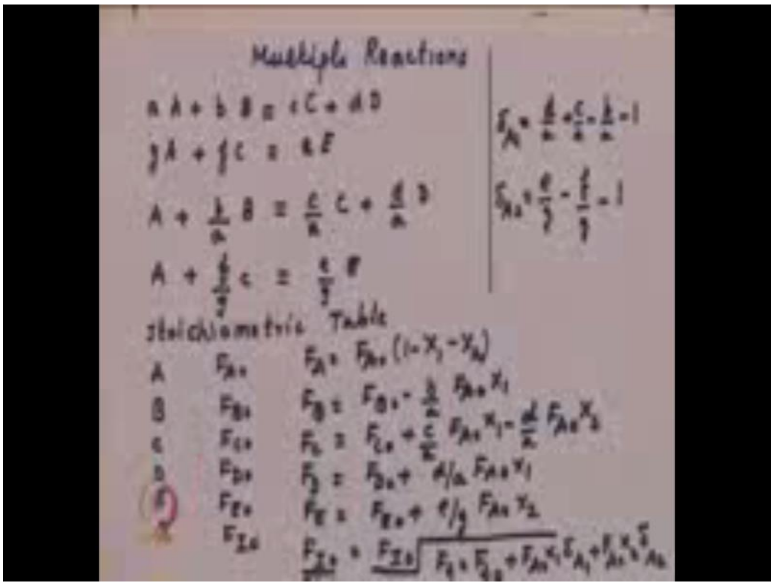

Multiple Reactions

Stoichiometric Table

I just taken an example where there are 2 reaction, we want to write a stichometry for the case of 2 reactions taking place. Now, that lot of material written here but, let me just run through this quickly A reaction B to gives C and D co efficiency a b C d given. Again A reacts with C to form another product so there are 2 reaction taking place. So, taking A as the basis have written here A plus b by a B is C by a C plus d by a D and similarly, A F by g C equal to E by G. So, when you write this stichometry which means what happens to all this species A B C D E and I and so on. So, these are the input values all these the input values. And these are the values at any instant where the conversions are whatever they are. So, what I have done is at since component a is reacting in reaction 1 and component a is reacting in reaction 2. So, I have taken let x 1 and x 2 b the fraction of a that reacts in 1 and 2 that is why say that the amount of A that remains unreacted is the amount of way that you put in multiplied by 1 minus of x 1 minus of x 2.

This how we positive rate what is happening? Once we do this now, what happens to B? B is reacting by this reaction therefore, I have written what is the b unreacted is given by this. Similarly, the C formed C is form from reaction 1 and reaction 2 so C is form from reaction 1 C by a F A 0 x 1 C is consumed in reaction to they are put on minus sign. D is formed in reaction 1 so D is d by a F A 0 x 1, E is formed in reaction 2 therefore, the F A 0 x 2. So, in you add up all this we this gives us the F t 0 alright this is F t. And when you add up all this you get F t 0 here. And then there are 2 terms as you can see very clearly F A 0 x 1 which is multiplied by this stichometry co efficient involved in reaction

1. F A 0 x 2 which we which is a multiplied by this stichometry co efficient involved in reaction 2 where delta a 1 and delta a 2 is only what is written is essentially stichometry that is written which respective component a. So, the numbers of moles of that you will see and any ins any position in the equipment is what you start with multiplied by plus there are 2 terms 1 due to reaction 1; 1 due to reaction 2.

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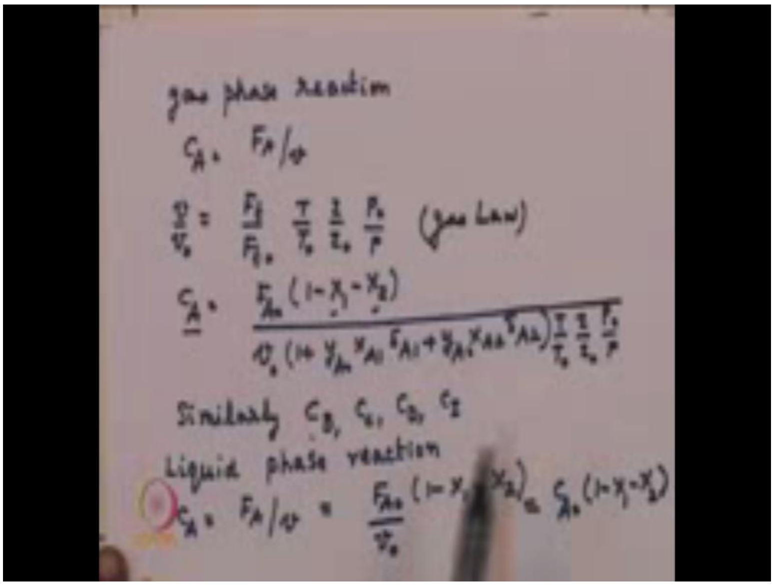

gas phase reaction

$C_A = F_A/v$

$\frac{v}{v_0} = \frac{F_t}{F_{t0}} \frac{T}{T_0} \frac{Z}{Z_0} \frac{P_0}{P}$ (gas Law)

$$C_A = \frac{F_{A0}(1-X_1-X_2)}{v_0(1+y_{A0}X_{A1}\varepsilon_{A1}+y_{A0}X_{A2}\varepsilon_{A2})\frac{T}{T_0}\frac{Z}{Z_0}\frac{P_0}{P}}$$

Similarly C_B, C_C, C_D, C_I

Liquid phase reaction

$$C_A = F_A/v = \frac{F_{A0}}{v_0}(1-X_1-X_2) = C_{A0}(1-X_1-X_2)$$

Moment of you have done that we recognize that we are able to now right what is the concentration of the species A B C D in the equipment why is it required? It is required, because of the rate function always given in terms of concentration therefore; we need to express concentration in terms of variable that we can measure. So, C A C A is F A by v we said this v by if this is the gas law this something that we know gas law. So, F t by F t 0 T by T 0 Z by Z 0 P 0 by P therefore, C A is what? F A 0 multiplied by whatever is the amount of a that is remaining the amount of a remaining is given by F A 0 1 minus of x 1 x 2.

Therefore, and then v 0 is what? v is v 0 times all this terms which takes into account the effect of temperature pressure and all that. So, this ratio essentially tells you how C A depends on x 1 and x 2 that is the moles once you can do for the component a it can do for any other component. So, we are able to express all the compositions A B C D in terms of 2 unknowns x 1 and x 2 what is the x 1 and what is the x 2? To be able to find out x 1 and x 2 you will go back and say how do we find out the x 1 and x 2? You have to make 2 measurements any 2 measurements if you make either on A and B that is enough to find out what is x 1 and x 2. Now, let us just to look at this in some detail.

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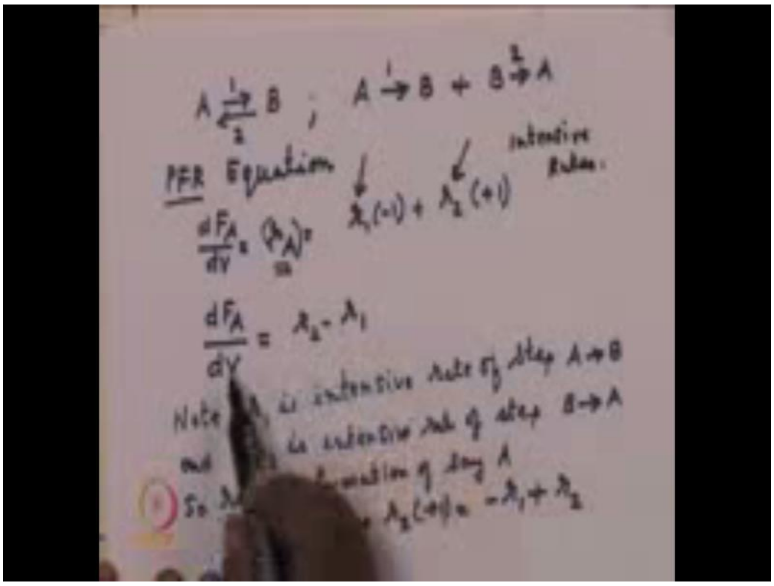

$A \underset{2}{\overset{1}{\rightleftarrows}} B \; ; \; A \xrightarrow{1} B + B \xrightarrow{2} A$

PFR Equation

intensive Rates.

$\frac{dF_A}{dV} = (r_A)_m = r_1(-1) + r_2(+1)$

$\frac{dF_A}{dV} = r_2 - r_1$

Note r_1 is intensive rate of step A → B

r_2 is intensive rate of step B → A

and formation of A

So $r_1(-1) + r_2(+1) = -r_1 + r_2$

Now, suppose we have a reaction like this A goes to B and B goes to A so we write it as reaction 1 and reaction 2. So, and we write our design equation for a plug flow in this form d by d v of F A is the rate of formation of component a. And component A is formed due to 2 reactions we say which is reaction 1 multiply plus and the reaction 2. But terms of r 1 and r 2 are the intensive rates of that 2 reactions what is meant by intensive rates? By intensive rates we mean there if you want to find out the rate of formation of A component you multiplied the intensive rate of that reaction by the appropriate stichometry co-efficient. So, if there are 2 reactions 1 and 2 you multiplied by appropriate stichometry co efficient to find the actual rated with that the particular component is formed. Therefore d F A d v becomes r 2 minus of r 1 and by extends 2 reason, because component A is form from reaction 2 and its consumed reaction 1 therefore, you get this.

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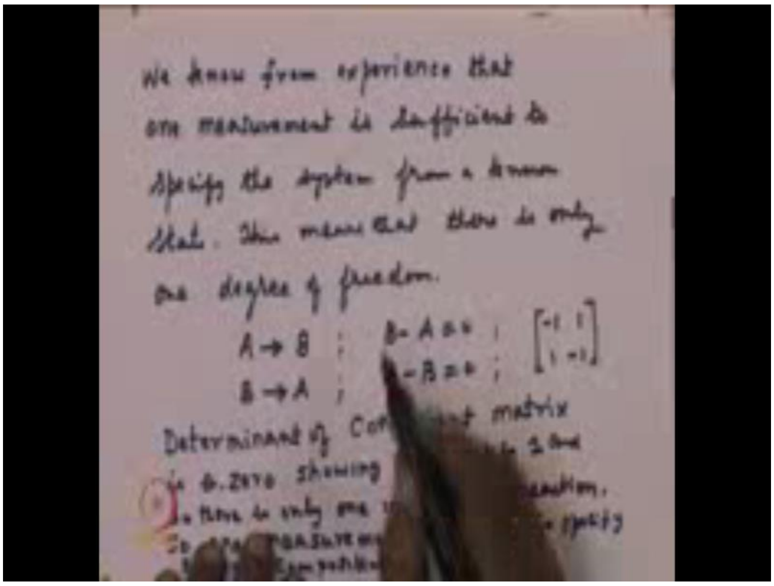

We know from experience that
one measurement is sufficient to
specify the system from a known
state. This means that there is only
one degree of freedom.

$A \to B$; $B - A = 0$; $\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}$
$B \to A$; $A - B = 0$;

Determinant of co[illegible] matrix [illegible]
is zero showing [illegible] reaction.
i.e. there is only one [illegible] specify
so one measurem[illegible]
[illegible] composition

So, what we are now, saying is that when there is the reaction like this A goes to B and B goes to A. And we express this in the form of 2 algebraic equations B minus A equal to 0 and A minus B equal to 0 we why do say this is B minus A equal to 0 are convention is products of positive co efficient and reactant have a negative stichometry co efficient. Therefore, we write first reaction is B minus A equal to 0 and second reaction is A minus B equal to 0. In express is in this matrix form we find that the determinant of matrix is 0 showing that they rank of its matrix is 1. So, what we are now saying is that if you have a set of algebraic equations as we have written down just now.

You can find out number of this algebraic equation which are independent or how many of these react of this equation that independent that will determine the number of reactions with are independent that is what is being said. Now, we write this reaction A goes to B, B goes to A in this form we find that rank of the co efficient matrix is 1 which means that there may be 2 rate processes. But there is only 1 independent reactions what is meant by independent reaction which means that you need to make only 1 measurement which is required to characterize that system given the initial state? If you know the initial state or the feed state you need to make only 1 measurements which that is what meant by there is rank is 1 or number of independent reaction is 1. So, what we are now, want to do is that use this idea for a multiplied reaction network like something like this.

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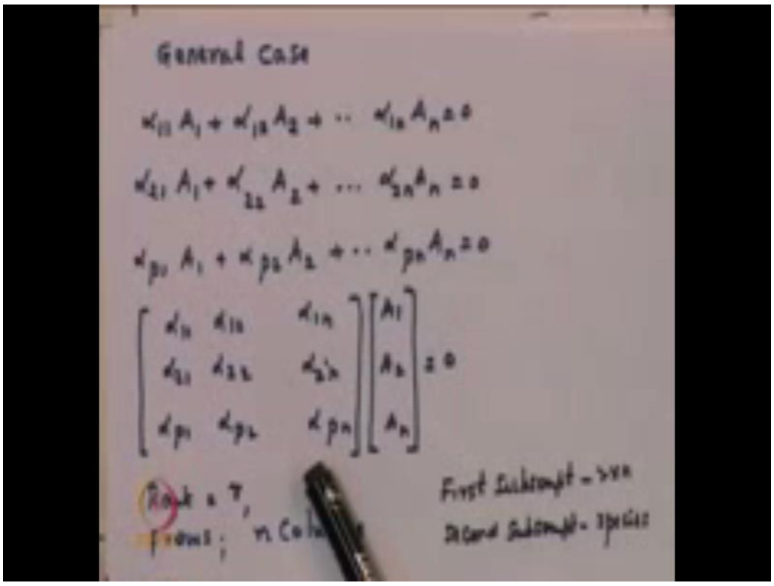

General Case

$$\alpha_{11} A_1 + \alpha_{12} A_2 + \cdots \alpha_{1n} A_n = 0$$

$$\alpha_{21} A_1 + \alpha_{22} A_2 + \cdots \alpha_{2n} A_n = 0$$

$$\alpha_{p1} A_1 + \alpha_{p2} A_2 + \cdots \alpha_{pn} A_n = 0$$

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \alpha_{2n} \\ \alpha_{p1} & \alpha_{p2} & \alpha_{pn} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_n \end{bmatrix} = 0$$

Rank = r,

p rows ; n Col

First Subscript = Rxn

Second Subscript = Species

That means you have a network which says alpha 1 1 A 1 alpha 1 2 A 2 up to alpha 1 equal to 0 like that there are p reactions. Notice here the first subscript is reaction the second subscript is species. So, when we say alpha 1 1 first reaction first species, alpha 1 2 is first reaction second species. This is the a nomenclature of writing a network of reactions. Now, when we express this is in the form of a what we call as the stichometry matrix which is alpha 1 1 to alpha 1 2 and alpha 1 n up to alpha 1 n to alpha p n. So, this matrix is this stichometry matrix. This matrix has determines what happens to this reactions therefore, the rank of this matrix will tell you how many reactions are independent. The rank will tell you how many of this reactions if the rank is r what does it mean? That in this network if you want to understand the composition of this system at any instant of time after beginning then you only has to a make r measurements. So, if you r measurements the entire n components system can be fully specified this always meant by the rank of this matrix Having said this so what is the that we have learn from this?

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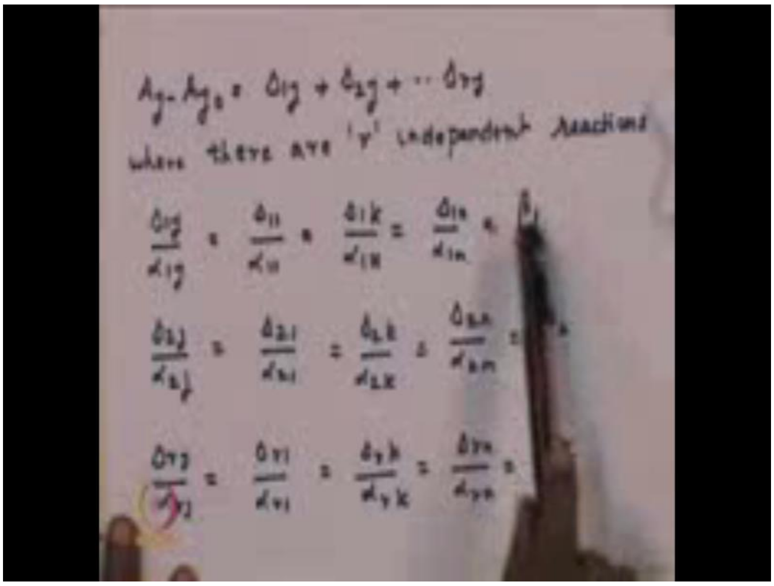

$$A_j - A_{j0} = \Delta_{1j} + \Delta_{2j} + \cdots \Delta_{rj}$$

where there are 'r' independent reactions

$$\frac{\Delta_{1j}}{\alpha_{1j}} = \frac{\Delta_{11}}{\alpha_{11}} = \frac{\Delta_{1k}}{\alpha_{1k}} = \frac{\Delta_{1n}}{\alpha_{1n}} = \beta_1$$

$$\frac{\Delta_{2j}}{\alpha_{2j}} = \frac{\Delta_{21}}{\alpha_{21}} = \frac{\Delta_{2k}}{\alpha_{2k}} = \frac{\Delta_{2n}}{\alpha_{2n}} =$$

$$\frac{\Delta_{rj}}{\alpha_{rj}} = \frac{\Delta_{r1}}{\alpha_{r1}} = \frac{\Delta_{rk}}{\alpha_{rk}} = \frac{\Delta_{rn}}{\alpha_{rn}} =$$

What we can learn from this is that if there is a component j if you have a component j. Therefore, A j minus of A j 0 represents change in this component j how can this change come up out? This change comes about, because there are r independent reactions and there is the contribution to this component j change, because of the each this independent reactions. What we are saying delta 1 j is the change in A j, because of reaction 1 delta 2 j is change due to reaction 2 similarly, delta r j is change due to reaction r. Now, we recognize that this term delta 1 j by alpha 1 j what is this mean?

Delta 1 j by alpha 1 j the change in component j in react due to reaction 1 alpha 1 j is the stichometry co efficient of component j in reaction 1. This is change due to reaction 1 this is the stichometry co efficient similarly, delta 1 n divided by alpha 1 n what is it? It is the change in component n due to reaction 1 and alpha 1 n is the stichometry co efficient of component n due to reaction 1. So, this ratio by definition is constant, because this is belongs to reaction 1 therefore, this equal to beta. Change due to reaction 1 component j divided by this stichometry co efficient of component j in reaction 1 that is the constant that we call us beta 1 similarly, for reaction 2 similarly, for reaction r. So, what is beta 1 beta 2 and beta r? These are change it exception these are the what are the units moles changes moles.

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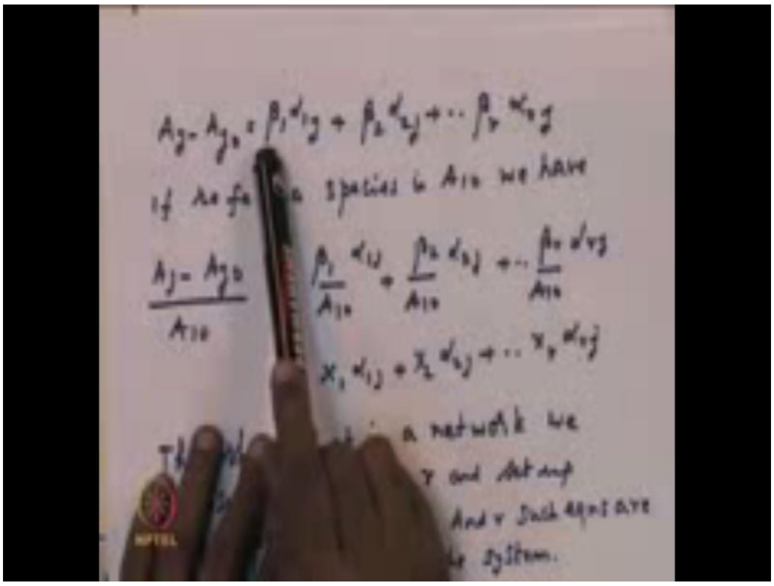

$$A_j - A_{j0} = \beta_1 \alpha_{1j} + \beta_2 \alpha_{2j} + \cdots \beta_r \alpha_{rj}$$

$$\frac{A_j - A_{j0}}{A_{10}} = \frac{\beta_1}{A_{10}} \alpha_{1j} + \frac{\beta_2}{A_{10}} \alpha_{2j} + \cdots \frac{\beta_r}{A_{10}} \alpha_{rj}$$

$$x_1 \alpha_{1j} + x_2 \alpha_{2j} + \cdots x_r \alpha_{rj}$$

So, with this relationship we recognize that this whole change A j minus of A j 0 can now, be written like this. We have written the what we have written this delta 1 j we can write it as delta 1 j is beta 1 times alpha 1 j. So, delta 1 j is beta 1 times alpha 1 j delta 2 j is beta 2 times alpha 2 j similarly, delta r j beta r times alpha r j. So, we are now, able to express the change in component j in terms of what we call as the smaller extent of reaction multiplied by the appropriate stichometry co efficient. Now, it is customer if our all of us to always to talk about reactions with respect to reference we are find it convenient. Because we are use to saying that the conversion is 50 percent 40 percent and 80 percent and so on. So, if we have a reference is much easy to comprehend what is going on.

Therefore, if we have a reference component A 1 0 with respect which want to understand the change in A j then you can divide throughout by A 1 0. So, that now, this term beta 1 by 1 this refers to change with respect to a reference species. There is an advantage in keeping a reference species, because it with respect that reference frequently or numbers can be made to go to 1. Because it is if we choose the reference appropriately other by you will go on go to 1. Therefore, by looking at reference component A j minus of A j 0 we are able to write in this form x 1 alpha 1 j x 2 alpha 2 j up to x r alpha r j. So, what is that we have done? By in appropriate definition we are able to express the change in A j A j minus A j 0 in terms which respect in a 1 0 in terms of x 1 alpha 1 j x 2 alpha 2 j x r alpha r j that r independent values of x of x 1 x 1 to x r.

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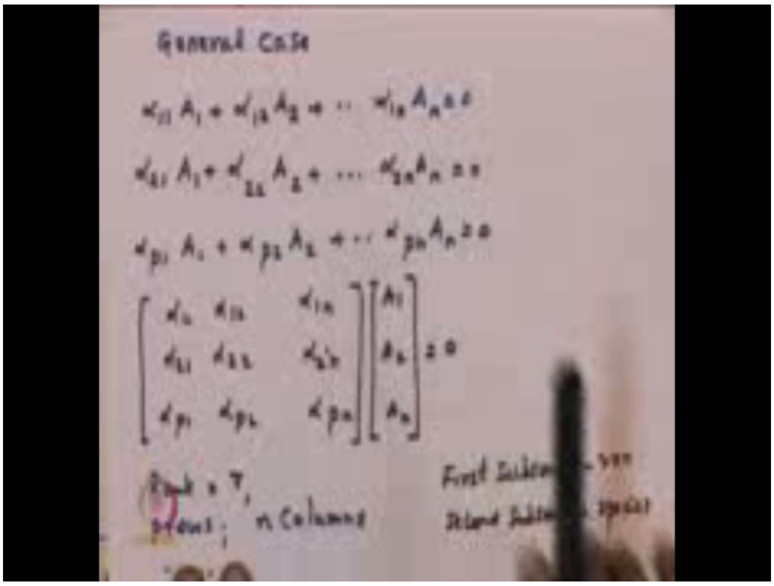

General Case

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$$\alpha_{21} A_1 + \alpha_{22} A_2 + \cdots \alpha_{2n} A_n = 0$$

$$\alpha_{p1} A_1 + \alpha_{p2} A_2 + \cdots \alpha_{pn} A_n = 0$$

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \alpha_{2n} \\ \alpha_{p1} & \alpha_{p2} & \alpha_{pn} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_n \end{bmatrix} = 0$$

Rank = r,

p rows ; n columns

So, what does it say here? That in a network we have to choose the set is after all we have a network. So, the rank is r which means what you have to choose from here a set r some reactions say may be 1 to 3 1 to 4 whatever. So, that that particular set that you have chosen must behave the rank r should not be different. So, we choose this set you choose must be a complete that is important. So, if you choosing the right kind of set so that the rank is r then you find that this the kind of relationship that we are set up works nicely for you change in A j is given by x 1 to x r multiplied by stichometry co efficient. See in this very important question the number of react rate processes are be the rate processes that are p rate process. If you recall I mentioned this little earlier how many rate process are here?

There are 2 rate process this only 1 independent reaction. Similarly, in a network you can have p rate process but, rank k p r and r is less than p delta 1 j by alpha 1 j what is meant by delta 1 j by alpha 1 j? Just let us look at that is once the reaction are I am just what is delta 1 j it is change in component j due to reaction 1 you are dividing that by alpha 1 j these stichometry co efficient of component j in reaction 1. So, this ratio is something unique to the reaction which is reaction 1 therefore, it must be equal for every component that participates in that reaction. That is where its delta 1 k divided by alpha 1 k. Every component that participates in that reaction this ratio is fixed.

Student: Sir the numbers of beta reactions are number of that

Number of reactions may be p, but the number of independent reaction of r and you need to take 1 to r reactions to understand the this is system. Because you do not need p measurement when you need only r measurements r is less than p. On other words what we are saying is that when there are 2 reactions see examples are that 2 reactions we need only 1 measurement. That is efficient to characterized this system the reason is the independent reaction are only 1.

Student: Sir r is the number of independent so r is the number of independent total number of reactions are independent

That is the number that is the procedure of finding out when you do matrix elimination you do done in your school I am sure we have do the matrix elimination. And elimination proceeds will you tell which of the reaction are independent. Because that we tell you by looking at that itself you telling reaction 1 to 2 3 are independent 2 4 5 are independent. The elimination procedure that may have been talk to otherwise we can talk about it, but it is not very difficult thing. So, is this is point clear what we are saying when we have a network of reactions there are r independent reactions. And then these are independent reaction x 1 to x r and therefore, you need only r measurements.

And therefore, if you want to find out the change in any component with respect to a reference this becomes what we have written here x 1 to x r multiplied by the appropriate stichometry co efficient. Now, advantage this techniques is that given species j we are able to write the species j in terms of the excess x 1 to x r therefore, it makes the network easier to deal with otherwise it is a little bit complicate. So, let us this illustrate this by an example illustrate this by this example we have chlorination of benzene what we have? We have chlorination of benzene. So, you have benzene reacts with chlorine to mono chloro benzene it gives to h C l benzene react mono chloro benzene reacts with chlorine give it chloro benzene dichloride with give it trichloro. So, you have component C is component1 b is component 2 b is component3 so all the components are listed.

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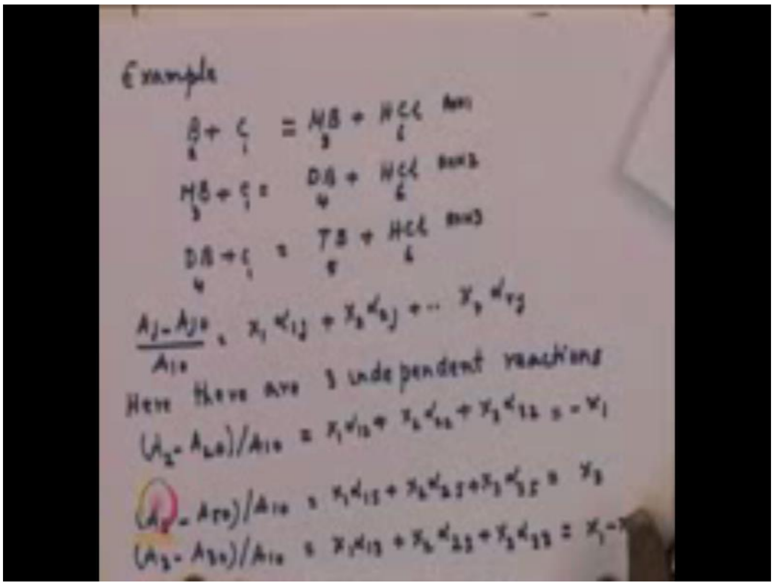

Example

$\underset{2}{B} + \underset{1}{C} = \underset{3}{MB} + \underset{6}{HCl}$ Rxn1

$\underset{3}{MB} + \underset{1}{C} = \underset{4}{DB} + \underset{6}{HCl}$ Rxn2

$\underset{4}{DB} + \underset{1}{C} = \underset{5}{TB} + \underset{6}{HCl}$ Rxn3

$\frac{A_j - A_{j0}}{A_{10}} = x_1\alpha_{1j} + x_2\alpha_{2j} + \dots x_r\alpha_{rj}$

Here there are 3 independent reactions

$(A_2 - A_{20})/A_{10} = x_1\alpha_{12} + x_2\alpha_{22} + x_3\alpha_{32} = -x_1$

$(A_5 - A_{50})/A_{10} = x_1\alpha_{15} + x_2\alpha_{25} + x_3\alpha_{35} = x_3$

$(A_3 - A_{30})/A_{10} = x_1\alpha_{13} + x_2\alpha_{23} + x_3\alpha_{33} = x_1 -$

Now, the question that we have to address is how do you write this stichometry table for this multiple reaction? We want to write this stichometry table and hence express concentration of all the relevant species in terms of conversion which we can measure how do we do this? So, what is done here is that we have written the material balance a j minus of A j 0 by A 1 0 equal to x 1 we just recall our equation here just A j minus the a j 0 is x 1 alpha 1 j x 2 alpha 2 j up to x r a alpha r how many independent reactions are here? We can say it is 3, because we have familiar with chlorination we have say it is x 3, but it may happened that we have determining the rank to be e sure in a situations which we are not very clear in may out determine the rank. In this particular case we know the answer therefore, the not term.

See the procedure for determination of rank there is the gauze elimination method is there you have will make all the diagonals 1 and below the diagonal 0. And here to count the number of diagonal which are 1 so it will be number of component is 6 the 6 components there are 4 reactions therefore, there are 4 1 2 3 4 and then 6 reactions. So, it will be 3 rows and 6 columns 3 rows and 3 rows 3 rows is that. Now, we go forward. So, what we are saying is that we can write our stichometry this form that means A 2 minus of A 2 0 I have taken A 2 minus of A 2 0 as an example this is given as x 1 alpha 1 2 x 2 alpha 2 2 x 3 alpha 3 3 is this clear what we are saying? So, what is the value of alpha 12? That is the value of alpha in reaction 1 component2 reaction 1 component2 what is the value of x? Alpha x minus 1 what is alpha 2 2? Reaction 2 component2 reaction 2 component2 is 0 0.

Now, alpha 3 3 x 3 what is the x 3 is not mentioned we are x 3 so what is the value of component2 in reaction 3? 0 therefore, it is minus of x 1. So, similarly, you do for component 5 you can do for all the component I have just taken only 3 component. Because the convenient so reaction 2 if A 5 here is A 5 0 divided by a 1 0 what is it? x 1 alpha 1 5 x 2 alpha 2 5 x 3 alpha 3 5 what is x alpha 1 5? 0 alpha 2 5, 0 alpha 3 5 0 what is plus 1? I have plus 1. Now, if you want to do this for A 3 minus of A 3 0 A 3 is what that is m so it is x 1 alpha 1 3 x 2 alpha 2 alpha 3 3. So, what are the values x 1 minus of x 2? On other word based on our stichometry we are able to express these species in terms of our unknown x 1 and x 2. This is the important point so what did say is that if you take what is a reference chlorine is our reference.

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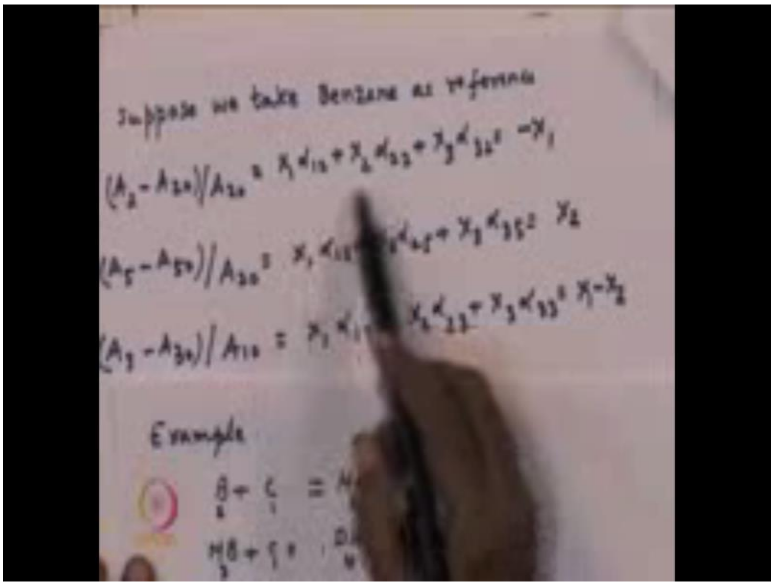

Suppose we take Benzene as reference

$(A_2 - A_{20})/A_{20} = x_1\alpha_{12} + x_2\alpha_{22} + x_3\alpha_{32} = -x_1$

$(A_5 - A_{50})/A_{20} = x_1\alpha_{15}$ [illegible] $\alpha_{25} + x_3\alpha_{35} = x_2$

$(A_3 - A_{30})/A_{10} = x_1\alpha_{1}$ [illegible] $x_2\alpha_{23} + x_3\alpha_{33} = x_1 - x_2$

Example

Suppose you take benzene as reference no harm is done. So, what we have done here a 2 minus a 2 0 x 1 alpha 1 2 and x 2 alpha 2 to x 3 alpha 3 2. So, what we are able to now do is that express A 2 A 5 in A 3 in terms of x 1 to x 3 multiplying the appropriate the stichometry co efficient. Now, let us illustrate 1 more problem so what we have try to do here is that if you have a multiple reaction you must be able to express your results using the standard procedure that is the most important.

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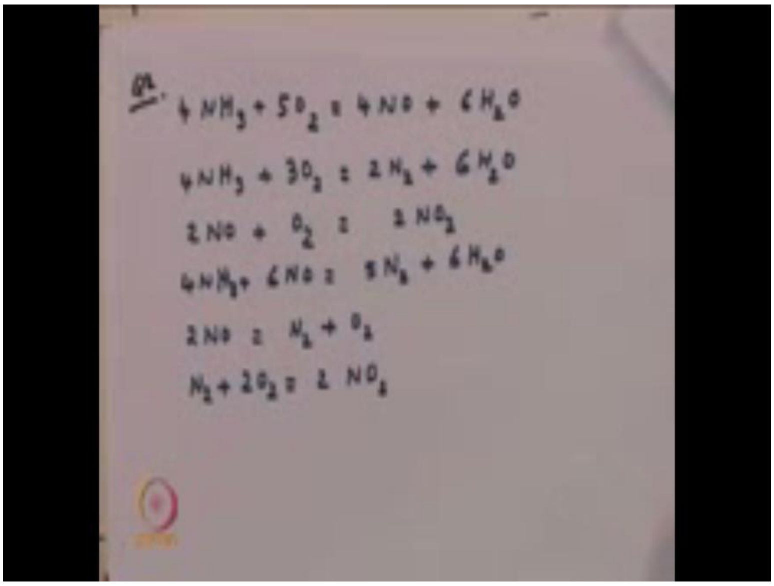

Q2. $4NH_3 + 5O_2 = 4NO + 6H_2O$

$4NH_3 + 3O_2 = 2N_2 + 6H_2O$

$2NO + O_2 = 2NO_2$

$4NH_3 + 6NO = 5N_2 + 6H_2O$

$2NO = N_2 + O_2$

$N_2 + 2O_2 = 2NO_2$

Now, this is Q 2 where we want to where we want to set up stichometry and then C where than we can set up the equation that are required to describe the process network how do you do this? When you get a monster like this you should first find the numbers of independent reactions how do you find the number of independent reaction? We said you have to make 0 along the diagonal by row manipulation and if that is the case the rank is the number of independent reaction you can see below the diagonal.

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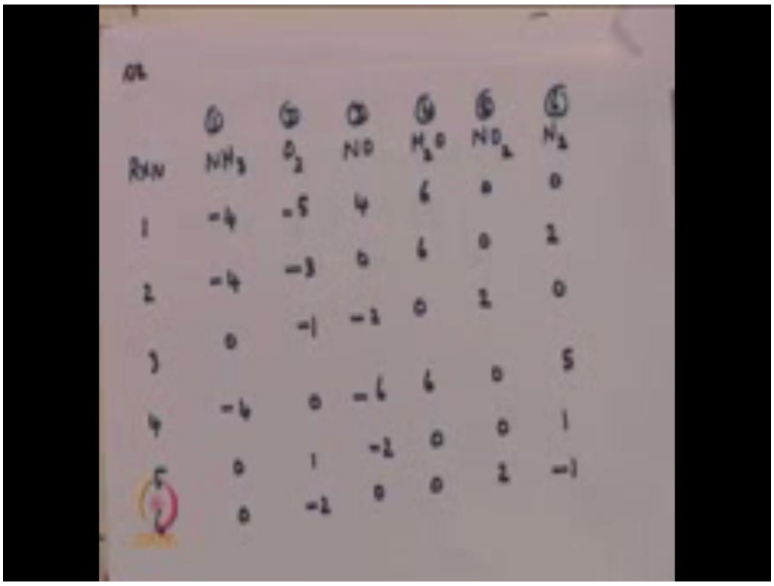

Q2

	①	②	③	④	⑤	⑥
RXN	NH_3	O_2	NO	H_2O	NO_2	N_2
1	-4	-5	4	6	0	0
2	-4	-3	0	6	0	2
3	0	-1	-2	0	2	0
4	-4	0	-6	6	0	5
5	0	1	-2	0	0	1
6	0	-2	0	0	2	-1

So, I have set up this matrix for this which looks like this ammonia, oxygen, nitrous oxide and water and N O 2 and nitrogen. So, how did I get this? I got this by putting the appropriate stichometry co efficient here I have put minus 4 means it will be minus 4 there is. Now, let us just look at these reactions. Reaction 1 gives you N O reaction 2 produces nitrogen. The reaction 3 produces nitrate, the reaction 4 produces what will produce reaction 4 ammonia 6 N O gives 5 H 2 6 balance is 10 occasions all right. Now, please recognize that there are some reactions which throughout nitrogen may be to the atmosphere. This reaction is also there this reaction positive related throughout into the atmosphere. So, this 4 N H 3 plus 3 O 2 there is nitrogen gas produced similar to what we talk to about so on the earlier stage. Now, what I want to do is I want to see after all if you want to do a design or if you want to do kinetic measurement you need to be able to relate what your collection to the equipment which we are done the experiment with. So, we have to generalize your result so that people again using.

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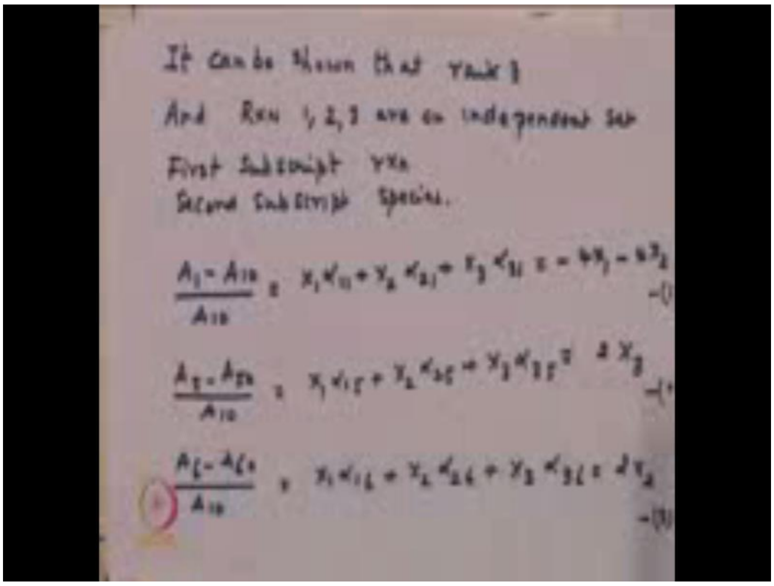

It can be shown that rank 3

And Rxn 1, 2, 3 are an independent set

First subscript rxn

Second subscript species.

$$\frac{A_1 - A_{10}}{A_{10}} = X_1\alpha_{11} + X_2\alpha_{21} + X_3\alpha_{31} = -4X_1 - 4X_2 \quad -(1)$$

$$\frac{A_5 - A_{50}}{A_{10}} = X_1\alpha_{15} + X_2\alpha_{25} + X_3\alpha_{35} = 2X_3 \quad -($$

$$\frac{A_6 - A_{60}}{A_{10}} = X_1\alpha_{16} + X_2\alpha_{26} + X_3\alpha_{36} = 2X_2 \quad -(3)$$

So, keeping that in mind what we have done is the written stichometry for A 1 A 5 and A 6 all these sets of equations.

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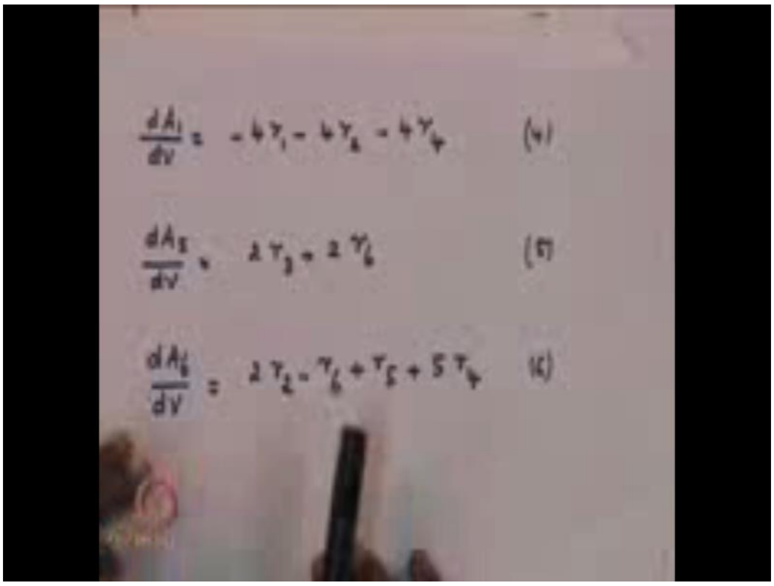

$$\frac{dA_1}{dV} = -4r_1 - 4r_2 - 4r_4 \quad (4)$$

$$\frac{dA_5}{dV} = 2r_3 - 2r_6 \quad (5)$$

$$\frac{dA_6}{dV} = 2r_2 - r_6 + r_5 + 5r_4 \quad (6)$$

For example, what is in that I have written? Based on this the rated to which A 1 changes with respected volume is given by minus 4 r 1 minus 4 2 minus 4 r 1 r 4 is it correct can you please tell me; d by d v of A 1 is it correct? Can we just check and tell me A 1 d by d v A 2 A 5 and A 6 tell me if it is how do we check this? In our material balance the left hand side is about what happens to our measurement? The right hand side is what happens to the reaction? So, the left hand side is d by d v A 1 it therefore, we can replace that from our stichometry table our right hand side of the rate processes. So, if I ask you which are the rate processes in which A 1 is involved A 1 is what? According to a 1 is ammonia so where the ammonia is is involved in reaction 1 reaction 2 reaction 3 so reaction 4.

So, it can say reaction 1 is minus 4 reaction 2 is minus 4 and reaction 4 is also minus 4. So, this stichometry co efficient of ammonia is minus 4 the reason is minus 4 is, because it is a reactant. So, similarly, we have written for other species. I have chosen A 1 5 and 6, because, I get some neat results, because our the result are very neat designs that it gives simple answers that is we have taken in like that. So, I have done this here please see if it is A 1 A 5 and A 6 gives as A 5 gives you to x 3 a 6 gives you x 2 and A 1 using this 2 you can eliminate x 2 you can get x 1. So, what we are able to do using the stichometry is that we are able to express our left hand side in terms of x 1 x 2 and x 3. A 1 depends upon x 1 x 2 A 5 depends upon x 3 and A 6 depends upon x 2.

So, the left hand side you are able to replace in terms of x 1 and x 2 and x 3 what is the right hand side this are the rate function r 1 r 2 r 3 r 4 r 5 r 6. We know that the rate functions depend upon concentration we know how to express concentration in terms of conversion? In this case in terms of x 1 to x r so the right hand side we know how to express in terms of x 1 to x r? The left hand side also we know how to express in terms of x 1 to x r? Therefore, you get and number of differential equations in x 1 to x r on the right hand side is the very non-linear function of x 1 to x r. But at v equal to 0 x 1 equal to 0 x r equal to 0 therefore, it is initial value problem where the initial state is specified. Therefore, you can forward integrate and get your results so when the final result looks something like this.

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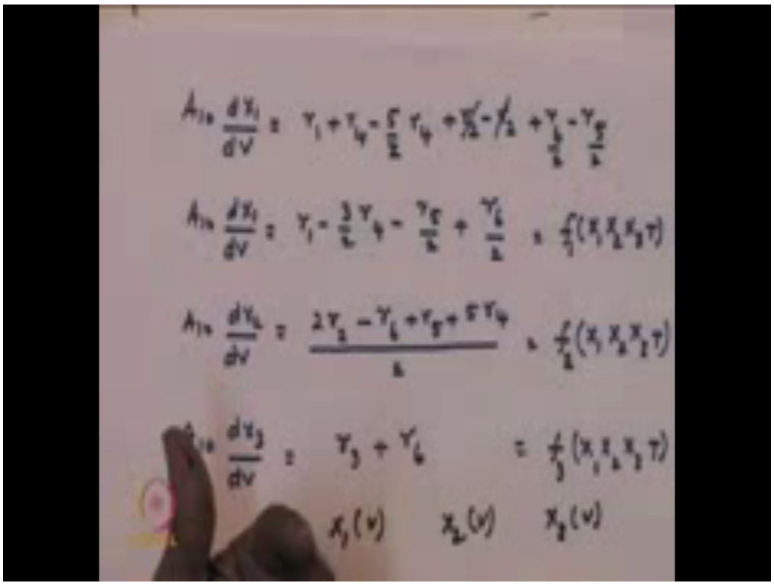

I have done the manipulation what it fines is that d x 1 by d v looks like this d x 2 by d v looks like this d x 3 by d v looks like this where the right hand side is the function of x 1 x 2 x 3 and temperature. So, these functions, how do you find out these functions? These functions come from an understanding of the rate process r 1 to r 6 for which data will be available. You should come from an independent set up measurements some people should have done. So, that the left hand side x 1 to x r is related to these functionalities which is known to you therefore, you can integrate forward. And then determine what happens to x 1 as the function of volume x 2 as the function of volume x 10 as the function of volume. Essentially what returns to you from this integration are these results? And this is what we want in a in a design are stimulation or in a in a control problem this is what we want. You want to tell what happens to x 1 x 2 and x r as we change our system. I will stop there.