Chemical Reaction Engineering

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Lecture No. # 02

Basic Concepts: Representations of Chemical Reactions

Friends, let us now start some serious discussion on chemical reaction engineering and we will do that by reviewing some of the undergraduate material. That is material; I was referring to in my last lecture in your first course on chemical reaction engineering. But before actually we do that, last time I forgot to mention something.

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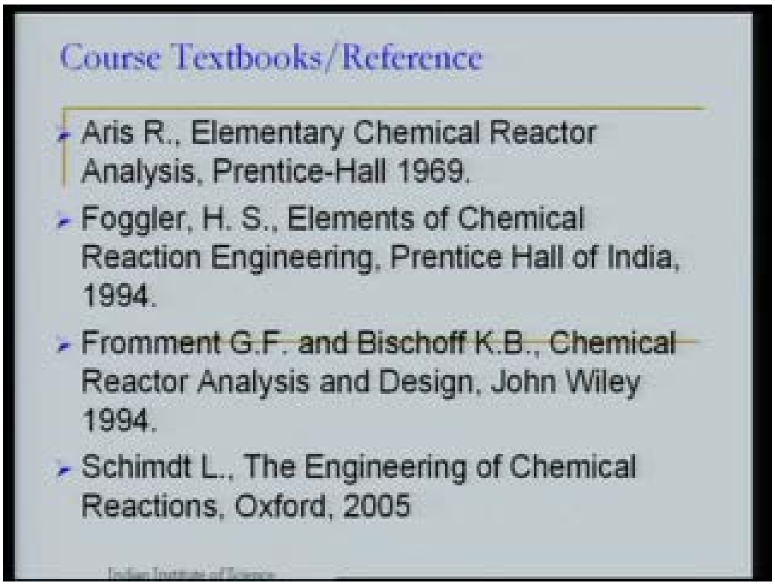

Course Textbooks/Reference

- Aris R., Elementary Chemical Reactor Analysis, Prentice-Hall 1969.
- Foggler, H. S., Elements of Chemical Reaction Engineering, Prentice Hall of India, 1994.
- Froment G.F. and Bischoff K.B., Chemical Reactor Analysis and Design, John Wiley 1994.
- Schimdt L., The Engineering of Chemical Reactions, Oxford, 2005

So, let me also highlight some of the good textbooks or reference books from which material for this lecture has been taken. The first book is a classical book by Aris, Aris was a mathematician turned chemical engineer on elementary chemical reactor analysis. The second book, you probably are all familiar with is the fabulous book on elements of chemical reaction engineering. And this is one of the books, where you have lot of material hands with which you can get hands on experience and so on. But more importantly it is available as an Indian eddition. So, it is affordable.

The third textbook which is also now available in India, is actually a graduate level book on chemical reactor analysis and design by formment and Bischoff. And the last book which I like is the book by lain Schimdt and you might have noticed few references in my last class to material from this book. This book is interesting not only because it gives very good analysis of chemical reaction, reactor design, and so on. But it is also good, because it gives lot of practical examples. The chemistry part which I was referring to, chemistry is important. So, there is lot of examples from real life chemistry examples and so it is always interesting to relate things to actual practice. So with this, now let us start reviewing some of the undergraduate material. What is this reaction engineering all about?

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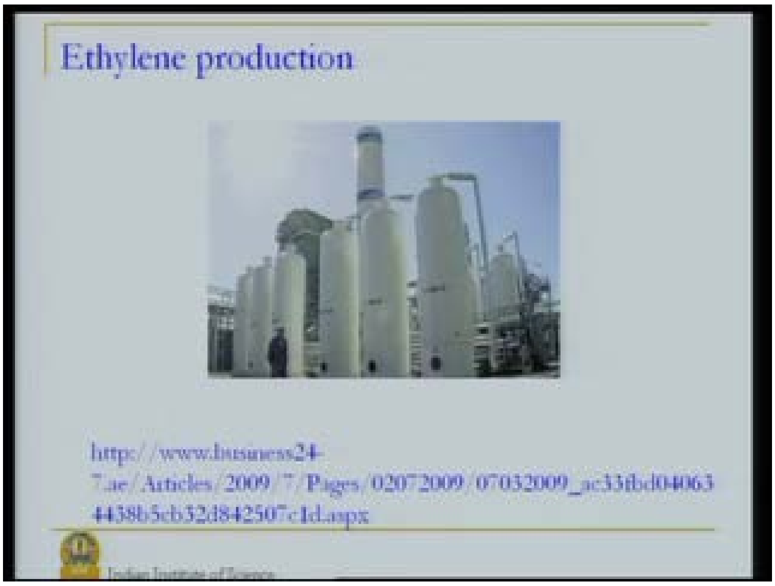

Ethylene production

http://www.business24-7.ae/Articles/2009/7/Pages/02072009/07032009_ac33fbd04063 4438b5cb32d842507c1d.aspx

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And let us take an example of ethylene production, what you see here is actually a plant which is coming up in Abudabi, which is going to produce about 10 about 1.5 million tons per annum of ethylene by steam cracking of ethane. So, while designing these reactors, what do we mean by designing these reactor. So, finally, at the end of this exercise something like this comes on.

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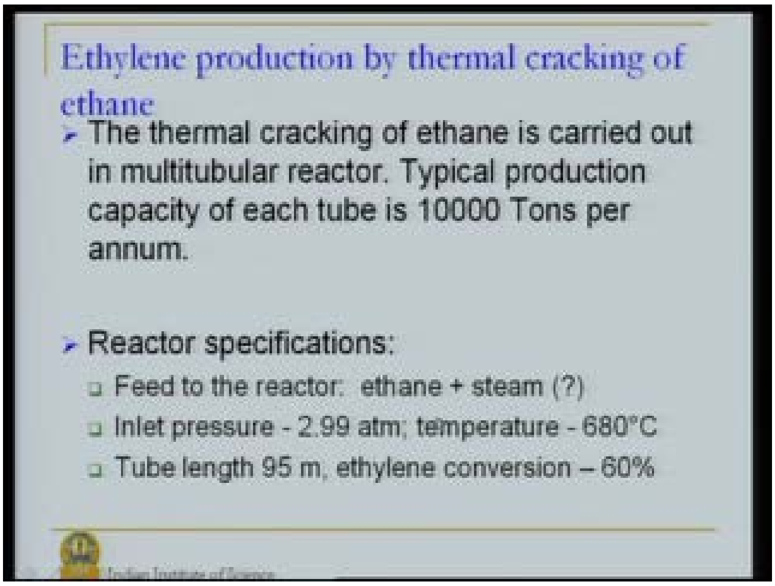

Ethylene production by thermal cracking of ethane

- The thermal cracking of ethane is carried out in multitubular reactor. Typical production capacity of each tube is 10000 Tons per annum.
- Reactor specifications:
  - Feed to the reactor: ethane + steam (?)
  - Inlet pressure - 2.99 atm; temperature - 680°C
  - Tube length 95 m, ethylene conversion – 60%

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So, let us say that we want to carry out this cracking of ethane. And typically, it is carried out in a tubular reactor, multi-tubular reactor. So, what you what you see here outside, as one long cell is actually having lot of tubes inside and some kind of a cell and tube kind of arrangement. So, we are going to produce ethylene in this reactor. And typical production capacity of each tube, I am not talking of each reactor that you saw in the previous photograph, but each tube is about 10,000 tons per annum. What happens in these reactors? So, some of the conditions that are specified is in the inlet of the reactor we have ethane and steam.

Now, you may be wondering why steam? Because steam actually does not participate in the reaction, the reaction is straightforward. Ethane looses one of one Hydrogen molecule to give ethylene. And so where does steam come into picture, we will try to find the answer to that question in due course. Then for example, the feed inlet pressure is about 3 atmospheres, temperature is about 600 degrees or 700 degrees centigrade.

Now, who told has to have inlet pressure of 3 atmospheres and temperature of 700, why not hundred atmospheres and ambient temperature. We will try to find the answer to this question as well. Then we have a tube length of about 95 meters and ethylene conversion or conversion of ethane for example, about 60 percent from the entry to the exit. So, these are all typical designed conditions that we have we have determined.

Now, how do we come across all these conditions? We will try to review the material that we have already seen which will partially answer these questions and in due course of time some new questions will be posed and of course, answered.

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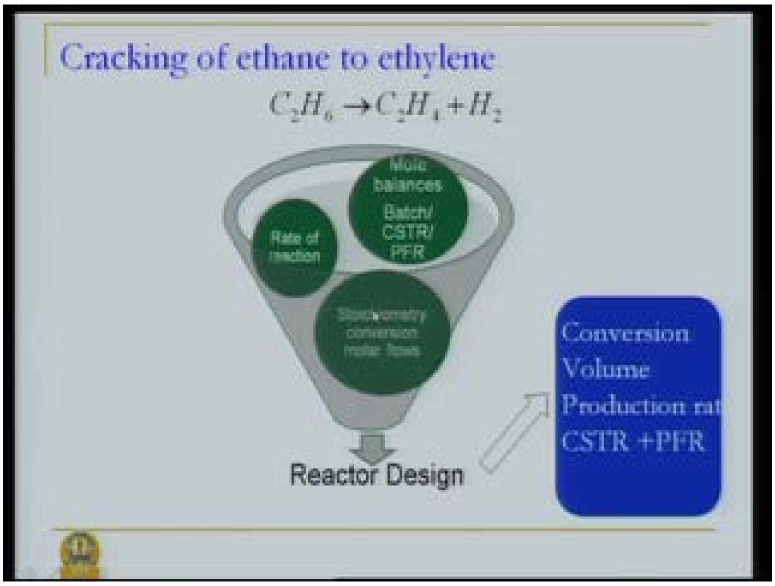

Cracking of ethane to ethylene

$C_2H_6 \rightarrow C_2H_4 + H_2$

Mole balances Batch/ CSTR/ PFR

Rate of reaction

Stoichiometry conversion molar flows

Reactor Design

Conversion
Volume
Production rat
CSTR +PFR

How do we go about reactor design, in general? So, this is our cracking of ethane to ethylene. So, we have one molecule of ethane giving rise to one molecule of ethylene and liberating one hydrogen, so that is a dehydrogenation reaction.

In a reactor design, what we what we typically do and this you would have seen in some form or the other. Is start with, what is the strychometry this reaction that is one molecule of ethane going to 1 molecule of ethylene and so on. What is the conversion? What are the molar flow rates that are going in and out of these reactors? Develop some suitable kinetics of this process.

So, that we know what is the rate of reaction. Put these two pieces of information together in the form of mole balances. Depending on the kind of reactor, whether we are doing a batch reactor or a C S T R or a plug flow reactor, there will be suitable mole balances and design equations. So, put these all these information together and then come up with the reactor design. The reactor design per say involves conversion finding conversion or finding volume of the reactor or length of the reactor, as we saw in the case of ethylene.

What should be production rate? What kind of reactors we should use and so on. So, these are our design criteria, I do not mean to imply that for every problem, all these will be considered. For example, in some problem we will be given that we want 60 percent conversion. What should be the volume of the reactor? Or if you have an existing reactor of certain volume, what is the maximum conversion that is possible and so on. So, we have various different combinations of these all these different things. So, the starting point for us is this strychometry and we will try to now represent our reaction in the more formal manner.

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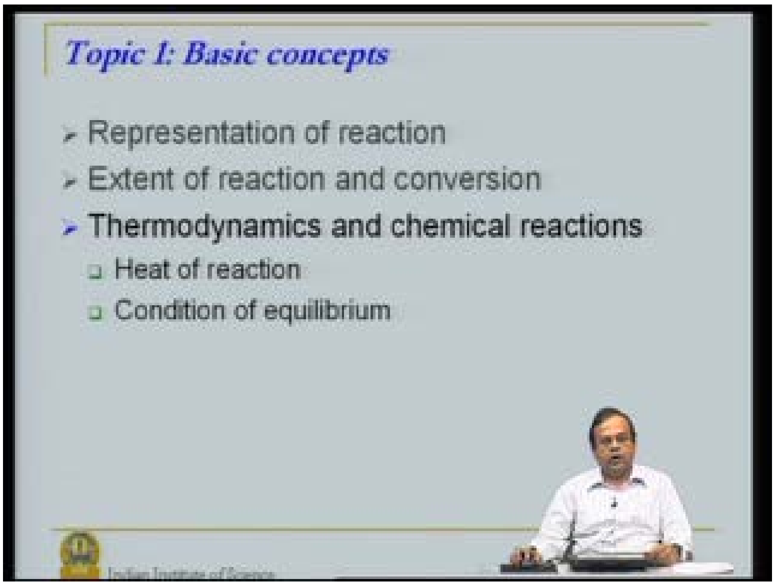

Topic I: Basic concepts

- Representation of reaction
- Extent of reaction and conversion
- Thermodynamics and chemical reactions
  - Heat of reaction
  - Condition of equilibrium

So, that we have the required stoichiometric tables and so on. Let us see how we represent a reaction. What I will be doing is giving you some kind of a general picture and then illustrating it with a particular example that is what I hope to do for all the lectures that we will be doing.

Then we will be looking at extent of reaction and conversion and some thermodynamics and chemical reactions. Thermodynamics is very important for reactions and we will try to see why they are important.

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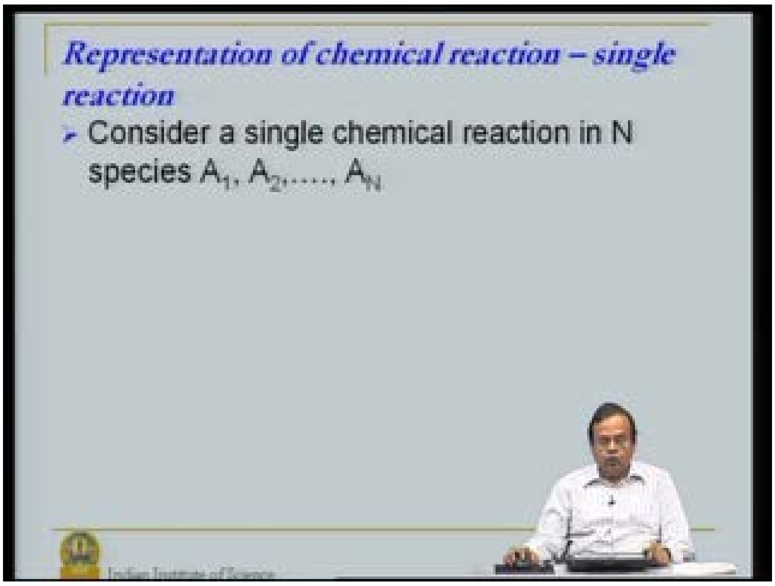

Representation of chemical reaction – single reaction

- Consider a single chemical reaction in N species A_1, A_2,…., A_N

So, let us start with the representation of a chemical reaction and we will start with the simplest possible way, we can do and namely consider a single reaction. Since we want to keep our discussion little general, as I said I will first start with first general definition and then I will go back to specific examples. And we will keep going back and forth. So, that we are together. Let us say that we have N number of different species. And we level them as A 1, A 2, A 3, A 4 and so on up to A N. and we now want to write a reaction of this. So, let us take an example of methanol synthesis.

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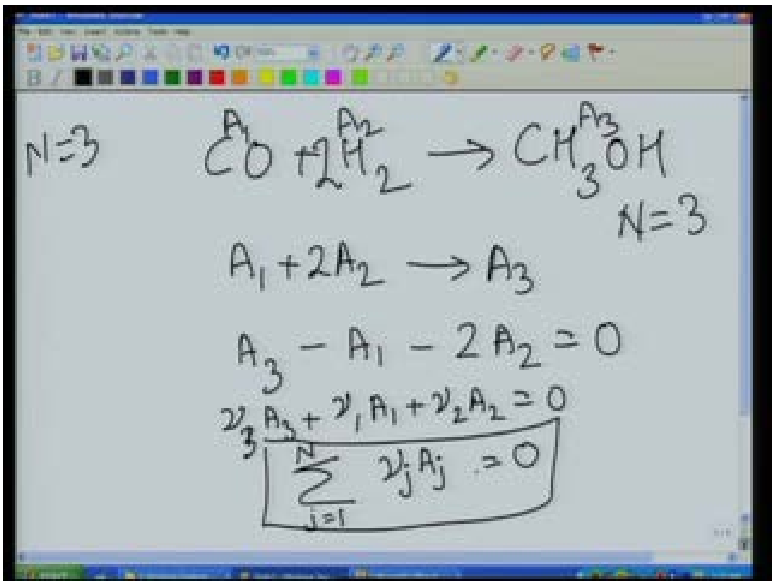

N=3

$$\overset{A_1}{CO} + 2\overset{A_2}{H_2} \rightarrow \overset{A_3}{CH_3OH}$$

N=3

$$A_1 + 2A_2 \rightarrow A_3$$

$$A_3 - A_1 - 2A_2 = 0$$

$$\nu_3 A_3 + \nu_1 A_1 + \nu_2 A_2 = 0$$

$$\boxed{\sum_{j=1}^{N} \nu_j A_j = 0}$$

Let us consider a reaction of Carbon monoxide and Hydrogen to give rise to methanol. And since this reaction has to be balanced, we need 2 moles of methanol, 2 moles of Hydrogen to give rise to 1 mole of methanol. Now, this reaction involves three species.
So, the N that we were talking in previously, N is 3. That is our numbers of species is 3 for this example and let us call this Carbon monoxide as A 1, Hydrogen as A 2 and methanol as A 3. So, I can immediately write these reactions as A 1 plus 2 A 2 giving rise to A 3. That is a standard way of representation, but to make our representation more uniform, I am going to write this same reaction in yet another form and that is A 3 minus A 1 minus 2 A 2 equal to 0. you will notice all I have done is, kept the product as it is and bring all reactants onto other side or from that is, what we normally write from left to right, I would just brought it on the other side. And return this reaction as A 3 minus A 1 minus 2 A 2 equal to equal to 0.

When I write these reaction like this, I can now write a stoichiometric coefficient nu 1 A 3 plus nu 3 A 3 plus nu 1 A 1 plus nu 2 A 2 equal to 0, as yet another representation.
All I have done is, I have generalized this reaction by converting this coefficients, which appear before A 1, A 2, A 3, in form of nu 1, nu 2, and nu 3 or in other words, I can write my generalized reaction now, containing species 3 species in this particular case A 1, A 2, and A 3 as summation of the product of the stoichiometric coefficient and the corresponding species. And summing it over all the species that are present in the

reaction and writing it, as summation nu j A j summation is over j going from 1 to 3 equal to 0.

Notice that I am making my representation more compact, as I am travelling down this slide. In general, if we have ten species I can write this reaction as j going from 1 to N summation nu j A j equal to 0. And this is my chemical reaction that I am going to focus on. The advantages of writing the reaction in this manner will become apparent as we as we continue our discussion.

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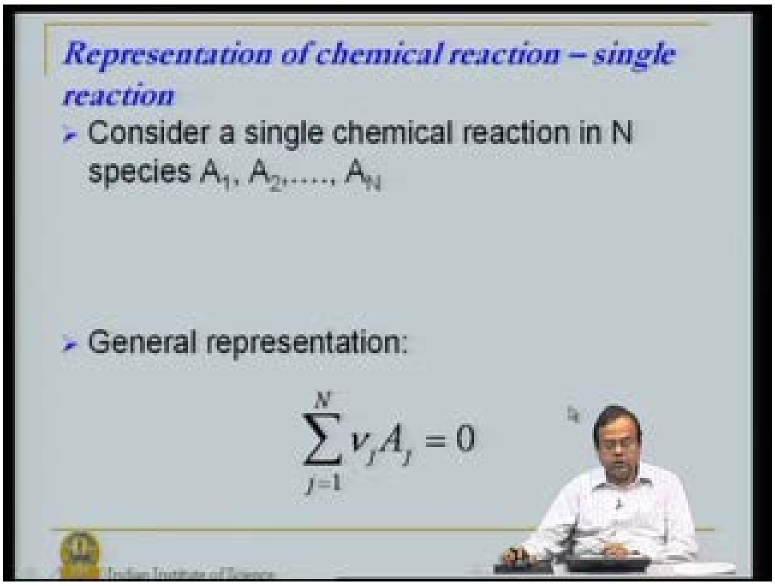

Representation of chemical reaction – single reaction

- Consider a single chemical reaction in N species $A_1, A_2, \ldots, A_N$
- General representation:

$$\sum_{j=1}^{N} \nu_j A_j = 0$$

Let us get back to our lecture. So, we have a single reaction between the N species A 1, A 2, A 3. And we just wrote these reactions in a general form, as summation nu j A j j going from 1 to N equal to equal to 0. So, that is our representation of my single reaction. Now, what happens if there are multiple reactions? And for that, what we will do is, let us say that I have this one reaction that that we started with.

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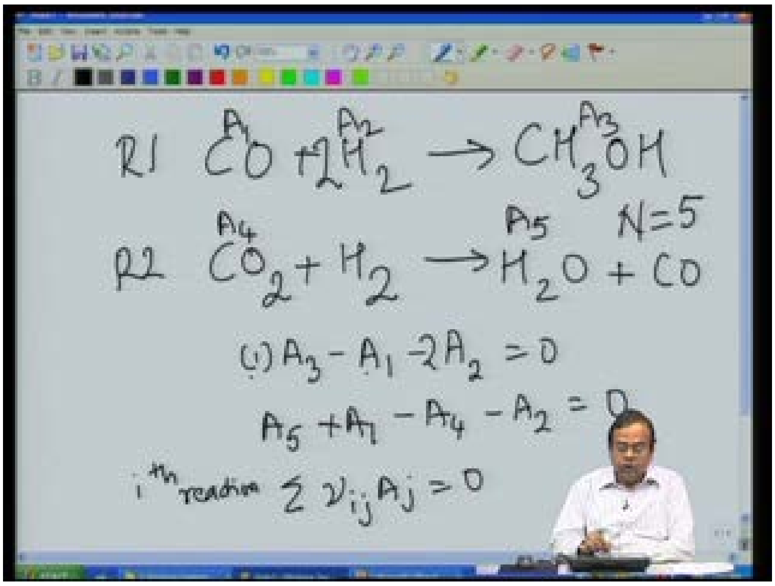

$R1 \quad \overset{A_1}{CO} + 2\overset{A_2}{H_2} \rightarrow \overset{A_3}{CH_3OH}$

$R2 \quad \overset{A_4}{CO_2} + H_2 \rightarrow \overset{A_5}{H_2O} + CO \qquad N=5$

$(i)\ A_3 - A_1 - 2A_2 = 0$

$A_5 + A_1 - A_4 - A_2 = 0$

i^{th} reaction $\sum \nu_{ij} A_j = 0$

So, let us label these reaction, I am going to call these reaction as reaction one and since it is reaction, I am just going to call it as R 1. Now, let us say that in this reacting mixture there was some C O 2 present in the in the reactor. And if that was present then there is a possibility that C O 2 may also react with Hydrogen giving rise to water plus Carbon monoxide.

Now, this is my second reaction. So now, I have two reactions which are possible and both reactions are possible simultaneously. So, this is a now case of multiple reactions, which is what actually happens typically in any real chemical reactor. you hardly ever have a single reaction. So, you have multiple reactions.

Notice here, that earlier we had three species. Now my number of species has increased, so I have to change this number. To account for the fact that there is another species Carbon dioxide and yet another species water, so my number of species is now five. So, I have five species Carbon monoxide, Hydrogen, methanol, Carbon dioxide, water. And between these five species there are 2 reactions R 1 and R 2.

Earlier we had written our first reaction as A 3 minus A 1 minus 2 A 2 equal to 0. The second reaction now, becomes A 5 and follows the same logic that is keep products as they are. So, A 5 plus A 1 bring the reactants on the other side. So, minus A 4 minus A 2 going to 0, as my second reaction. Now, what have we done? We have stoichiometric coefficients for all the species A 1, A 2, A 3 for the first reaction. Stoichiometric coefficient for all the species in the second reaction.

So, now I am going to define my stoichiometric coefficient, nu i j as the stoichiometric coefficient of species j in the ith reaction. So for example, if I am looking at nu 1 2, that is stoichiometric coefficient of my second species in first reaction. Second species which is Hydrogen, so my second species in the first reaction that is minus 2.

Similarly, I can define for all other species. So, for my ith reaction, I have a stoichiometric coefficient nu i j, which is for j th species in ith reaction. So, what is my ith reaction now? My ith reaction is nothing but summation nu I j A j equal to 0. So, that is my ith reaction. And so, this is my first reaction, second reaction and so on. Depending upon how howsoever reactions we have. Notice here, while defining our stoichiometric coefficients that is by writing reaction as left hand side equal to 0, we have followed one standard convention. Namely, if the reaction is if the species is the product of the reaction, namely like methanol, the stoichiometric coefficient is positive.

If the species is the reactant, the stoichiometric coefficient is negative. So, we follow this standard convention of positive stoichiometric coefficient for the product and negative stoichiometric coefficient for the reactor reactants. So, this is my general nth general ith reaction.

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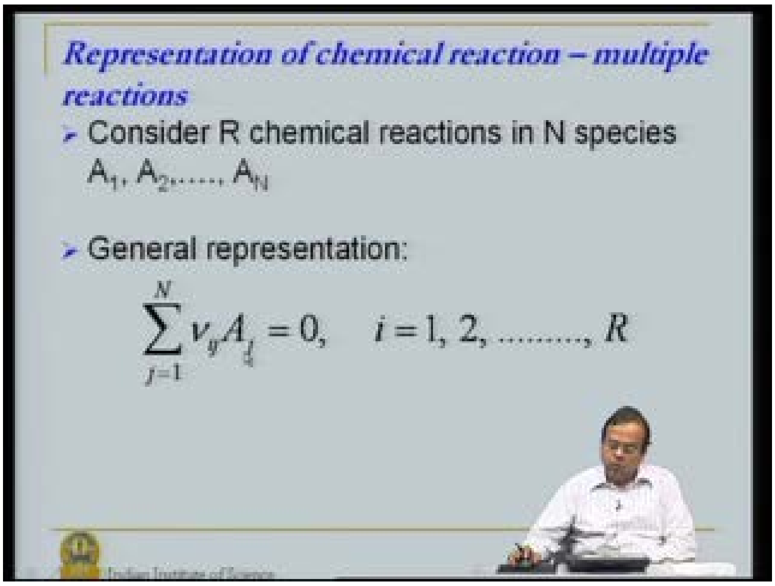

Representation of chemical reaction – multiple reactions

- Consider R chemical reactions in N species $A_1, A_2, \ldots, A_N$
- General representation:

$$\sum_{j=1}^{N} \nu_{ij} A_j = 0, \quad i = 1, 2, \ldots\ldots, R$$

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And we now, therefore have, for multiple reactions there is we are considering R chemical reactions in N species, so that between A 1, A 2, A 3, A N. and we write this general representation, as summation nu i j A j equal to 0, that is my ith reaction. So, I go from reaction 1, 2, and 3 up to, whatever R reaction that I have. That is from for species in this summation from j equal to 1 to N represents my ith reaction and we have R such reactions.

Once again the stoichiometric coefficient is positive, if the species is a product of the reaction. It is negative, if the species is the reactant in the reaction.

Now, let us play around with these species little more and say that we have yet another reaction. So, let us say that these are the two reactions in these five species. And I am going to consider, yet another reaction for my consideration, namely C O 2 plus 3 H 2 giving rise to C H 3 O H that is our methanol plus water.

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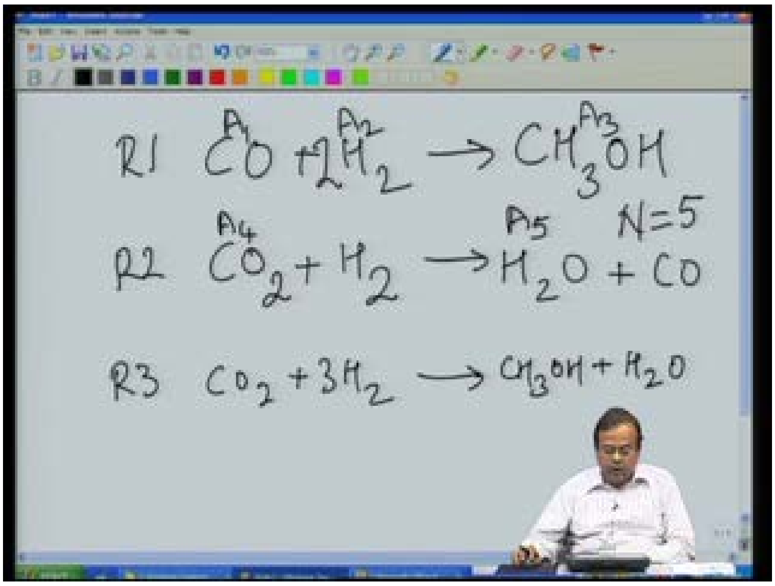

R1 $\overset{A_1}{CO} + 2\overset{A_2}{H_2} \rightarrow \overset{A_3}{CH_3OH}$

R2 $\overset{A_4}{CO_2} + H_2 \rightarrow \overset{A_5}{H_2O} + CO$ $N=5$

R3 $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

So, I am going to call this reaction 3. This species are still 5, but I have two reactions. I am going to write third reaction and you can think of many more reactions or reactions in many different ways, one can think of. Do we really need this third reaction? I think by now, you would have realized, the way I wrote this third reaction, this third reaction over here was just eyeing these two reactions and I wrote my third reaction. So, in that sense my third reaction is actually a sum of these two reactions or it is not an really an independent reaction, but is a dependent reaction, dependent on the other two reactions in the system.

We naturally do not want such dependent reactions. Because what is enough for us is the number of independent reactions, because any other reaction can always be written as a combination of the remaining reactions. So, how do we find out, whether the given reaction. Suppose, I am given this set of reaction and I want to find out, is this reaction, are these all three reactions independent or there is some dependency of one reaction on other two reactions. Is this really an independent reaction or is it a dependent reaction.

So, how do I find that out? I find that out by going back to my mathematical representation of multiple reactions and focusing on this stoichiometric coefficient. In fact, we can write this stoichiometric coefficients for all reactions put together in a matrix form.

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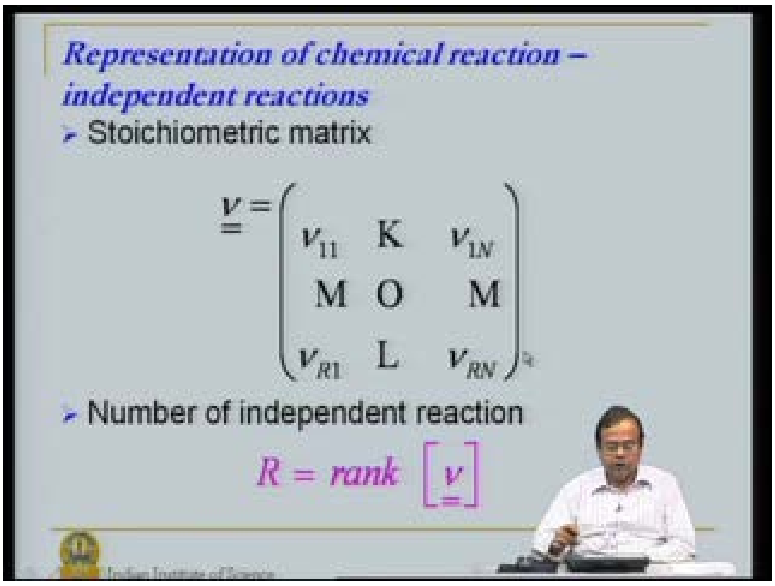

Representation of chemical reaction – independent reactions

- Stoichiometric matrix

$$\underline{\underline{\nu}} = \begin{pmatrix} \nu_{11} & K & \nu_{1N} \\ M & O & M \\ \nu_{R1} & L & \nu_{RN} \end{pmatrix}$$

- Number of independent reaction

$$R = rank \left[\underline{\underline{\nu}} \right]$$

That is stoichiometric coefficients, so what I have here, is a row representing each of the reactions. So, this is reaction 1, this is reaction 2, this is reaction 3 and so on. And on the columns, I have species 1, 2, 3, 4, 5 up to N. So, for our example that we previously saw, this is my first reaction, this is my second reaction, that is reaction between Carbon monoxide and Hydrogen. This is my second reaction let us say, between Carbon dioxide and Hydrogen. And this is my third reaction, which is between Carbon dioxide and Hydrogen.

Recall, we had written this third reaction as sum of these two reactions. For those who are mathematically inclined, you would have now figured out, the way to find out the independent reactions. How I repeat my third reaction is sum of the first two reactions. Or in other words, my third row of this matrix, what is the dimension of this matrix? It is R by N. my third reaction or my third row rather, is dependent on first two rows and when you have a matrix and when any one column or when any one row is a linear combination of other two rows, we always think of rank of these matrix.

The rank of this matrix, stoichiometric matrix nu is actually the number of independent reactions. So, if you go back to our set of reactions, write this matrix and try to find the rank. What rank do you expect? You expect rank to be 2. That means, there are only two independent reactions and we need not consider the third reaction. It is important that we consider only independent reactions and reasons for these are meaningful.

For example, if you are any mass balance or mole balance or any other analysis with this stoichiometric matrix. Why have something more than what you need? First of all, if you had A 3 by 3 matrix by considering only independent reactions. we would have reduced it to 2 by 3 and reducing dimensionality always is of great help. But there is another recent use of these stoichiometric matrixes and its rank. And it comes from a very unlikely source, namely you and me or to make it broad living cells. What happens inside the living cells is there are numerous species. And by numerous, I mean hundreds and thousands of species involved in numerous reactions, again hundreds and thousands of this reaction.

So in principle, one can setup a stoichiometric matrix of this kind. And believe me these are all pure chemical reactions, while we may call them as biochemical reactions, because they are occurring in biological systems, but these are chemical reactions. So, we have this strychometry for all such reactions. And once you write this stoichiometric matrix, this matrix gives you lot of useful information about, what is happening inside the cell. It tells you for example, to give you just quickly the idea, if we say that our third reaction is dependent on first and second reaction. Then suppose third reaction is addition of first and second reaction then we also know that, the rate of third reaction must be rate of first reaction and second reaction. Or in other words, if we are presented with such a matrix, it is enough to measure rates of these two reactions will always get the rate of the third reaction.

So, information of this kind which is all put together, one say something what is called as metabolic engineering, flux analysis, metabolic control analysis. These are some of the some of the fields in which this stoichiometric matrix is extensively used.

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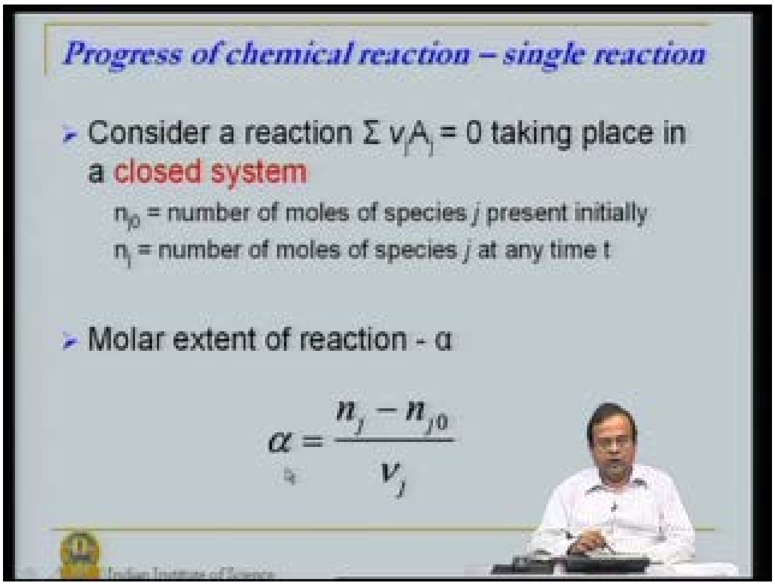

Progress of chemical reaction – single reaction

- Consider a reaction $\Sigma \nu_j A_j = 0$ taking place in a closed system
  - n_{j0} = number of moles of species *j* present initially
  - n_j = number of moles of species *j* at any time t
- Molar extent of reaction - α

$$\alpha = \frac{n_j - n_{j0}}{\nu_j}$$

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So, now we move on to another idea. That is we know how to write our reaction. And let us now go forward and actually do this reaction. and I want to know how far has this reaction progressed. So, I want to know the progress of this chemical reaction. I will again start with a single reaction and then we will extend the idea for multiple reactions. So, how do we measure chemical reaction?

So, the idea here is the following, now let us consider once again, a single reaction summation nu j A j equal to 0. I omitted summation j for sake of simplicity, but it is understood that it summed over all species. And let us say that this reaction is taking place in a close system. I underlined this idea that is it is a close system that is there is no exchange of matter of this system with this surrounding, that is what we understand by a close system.

So, let us say that I am carrying out this reaction in a closed system. I started out my reaction having n j 0 moles of species j in the initial start up of the reaction. So, I have species A j and there are n such species capital N and small n is what I use to note denote the number of moles of these species j and another subscript 0 to note that, it is initially present. And then, let us say that these reaction progresses for some time t and at the end of this time the number of moles of species j left in the reactor are n j.

So, we have two measures, moles initially present, moles present at time t. Then I define my extent of reaction, molar extent of reaction alpha as a major of progress of my reaction. And how is alpha defined? Alpha is defined as the ratio of the difference between the moles present at any time t n j minus, what we started out with and ratio of this difference. So, this is actually how much has changed in the reaction from its starting point to the stoichiometric coefficient of this species A j that is nu j.

Let me repeat, molar extent of reaction alpha is defined as change in number of moles of species j that is n j minus n j 0 divided by nu j, the stoichiometric coefficient and this is my first measure of progress of reaction.

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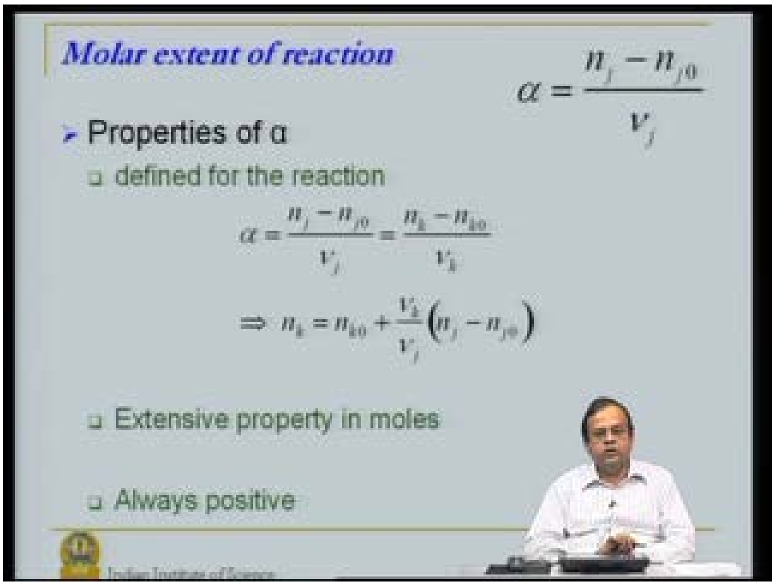

Molar extent of reaction

$$\alpha = \frac{n_j - n_{j0}}{\nu_j}$$

- Properties of α
  - defined for the reaction

$$\alpha = \frac{n_j - n_{j0}}{\nu_j} = \frac{n_k - n_{k0}}{\nu_k}$$

$$\Rightarrow n_k = n_{k0} + \frac{\nu_k}{\nu_j}\left(n_j - n_{j0}\right)$$

  - Extensive property in moles
  - Always positive

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Let us look at some of the interesting properties of this extent of reaction. Once again, this is the definition of my extent of reaction. I want you to focus on the fact that I am always saying molar extent of reaction. That is I am talking about a reaction now, not a species. In other words, this quantity alpha is defined for the reaction and not for the species. So, I could choose to write alpha as n j minus n j 0 by nu j, for j th species or n k minus n k 0 by nu k, for k th species and so on. And these all must be same, because it is the same reactions that we are referring to.

Since, it is not alpha is not defined for the species, but for the reaction, I can use this quantity n j minus n j 0 by nu j or n k minus n k 0 by nu k n l minus n l 0 by nu l and so on. And they all must be equal. By using this equality and rearranging these terms, I can write now the number of moles of species k, at any point of time is what we started out with n k 0 plus, the ratio of nu k by nu j the corresponding stoichiometric coefficients into the difference between n j minus n j 0.

So, what has happened now? What we have done is we have defined the extent of reaction used the fact that these are not specific to any particular species, but for a reaction. And now return, the moles of species k in terms of difference in moles of species j. And this can be done for all species 1 2, suppose, we choose j as 1. So, n 1 minus n 1 0 into nu k by nu 1 plus n k 0 will be n k. And this k will be for all 2, 3, 4, 5, 6 and so on. Or in other words, we can relate the change in number of moles of all species through this stoichiometric coefficients or stoichiometric relations. So, we have n k as n k 0 into nu j nu k by nu j n j minus n j 0.

Going back to this extent of reaction. Notice that, at the start of this reaction n j is same as n j 0. And as you would expect reaction has not progressed, that means, alpha is 0, at a beginning of the reaction. As the reaction proceeds n j is different than n j 0. Let us say, that species j that we are looking at is Carbon monoxide or the reactant. So, if it is reactant n j will be less than n j 0, because Carbon monoxide has got reactant. So, this numerator will be negative. But so is the denominator, because since species j or Carbon monoxide in our example, is reactant the stoichiometric coefficient is negative.

So, we have a ratio of negative to negative quantities, which means alpha is positive. You can argue the same thing, if j is product. Numerator will be positive, denominator will be positive or in other words, alpha is always positive. It is 0 in the beginning, it is positive for rest of the time that reaction is taking place. Alpha that is the extent of reaction is also an extensive property. That is it is related to the mass of the system. It is an extensive; you know in thermodynamics you have studied intensive properties and extensive properties. Alpha is one of the extensive properties, because it is in moles, so mass associated with mass.

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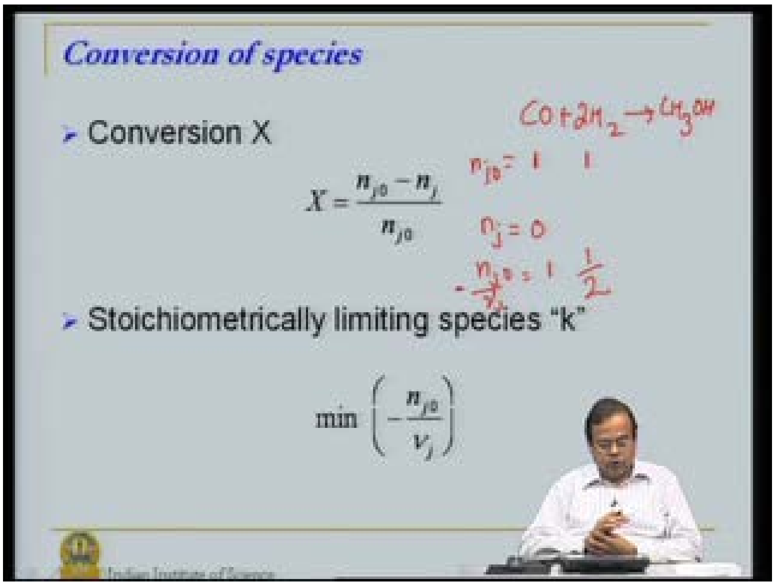

Conversion of species

- Conversion X

$$X = \frac{n_{j0} - n_j}{n_{j0}}$$

$CO + 2H_2 \rightarrow CH_3OH$

$n_{j0} = 1 \quad 1$

$n_j = 0$

$-\frac{n_{j0}}{\nu_j} = 1 \quad \frac{1}{2}$

- Stoichiometrically limiting species “k”

$$\min\left(-\frac{n_{j0}}{\nu_j}\right)$$

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Now, you may ask, what happens if we have more than one reaction? We will come back to our multiple reactions little later. But let us define now, another progress measure of progress of reaction, namely the conversion of the species. And we define conversion X, again for the same reaction summation nu j A j equal to 0, that is my general reaction.

I define my conversion as X as n j 0 minus n j divided by n j 0. I am now defining conversion for a species; I am no longer defining for a reaction, but for a species as n j 0 minus n j divided by n j 0. Let us say that Carbon monoxide is the species that we are referring to. My conversion of Carbon monoxide is the initial moles of Carbon monoxide; I had minus the current moles divided by the initial moles. And this quantity conversion X goes from 0 to 1. It is 0 at the beginning and at best, it can be 1.

Now, we will see the cases where conversion will never reach 1 and perhaps some of you guessed it right. When it is a reversible reaction, your conversions may never go to 1. Or in terms of percentage, you may never have 100 percent conversion of your reactant. But, that is a subject for our next class, what happens when you have reversible reactions?

For time being, let us say that it does go up to 1. So, we are dealing with an irreversible reaction. Now, once again the conversion is tied down to species, unlike our extent of reaction which was tied down to the reaction. The moment we say that our conversion is related to species, the question arises which species? Is it same for all species or we define only for one particular species. conversion is typically divided for only what we call stoichiometrically limiting species K. That is, it is defined for that species K which is stoichiometrically limiting. What do I mean by stoichiometrically limiting species?

So, let us go back to our example of Carbon monoxide plus hydrogen giving rise to methanol. So, in principle, I can define conversion for both Carbon monoxide and hydrogen in this example. But I am going to do it with basically, one of the species which is limiting. Now, how do I decide that limiting species? The idea is very simple, let us say that we started with 1 mole each of Carbon monoxide and hydrogen. So, my n j 0 was n j 0 was 1 for both these both these species.

Now, can I get for example, for Carbon monoxide n j equal to 0. That means, can I have complete conversion of Carbon monoxide. No, because if you look at the stoichiometric coefficients of Carbon monoxide and hydrogen. To completely consume 1 mole of Carbon monoxide, I need 2 moles of hydrogen, but I had only 1 mole. That means, in this example my hydrogen is the limiting species, because my reaction will stop moment my hydrogen is exhausted from the system. And therefore, I refer to hydrogen as my species K that is the limiting species. How do I find out which is limiting? So, how did we find that hydrogen is limiting? So, we look at the ratio of n j 0 and nu j.

So for example, n j 0 by nu j for Carbon monoxide and negative of that would be 1 and for hydrogen, it will be half. That is 1 mole we started with stoichiometric equation 2. And we look for minimum of these ratios, one half. If there are more species, we will look at each of these ratios n j 0 by nu j and the minimum ratio, that is the ratio for the species for which this ratio this quantity is minimum is my limiting species.

So, I have now a concept of limiting species. And this conversion is referred to, in terms of that limiting species. So for example, if this was the conditions under, which I am doing this reaction, 1 mole of Carbon monoxide and 1 mole of hydrogen. My limiting species is Hydrogen. And moment it gets hundred percent converted, the reaction will stop. There would not be complete conversion of Carbon monoxide, because 0.5 moles of Carbon monoxide will still be remaining. Because 1 mole of hydrogen can only utilize 0.5 moles of Carbon mono and we will get only 0.5 moles of hydrogen.

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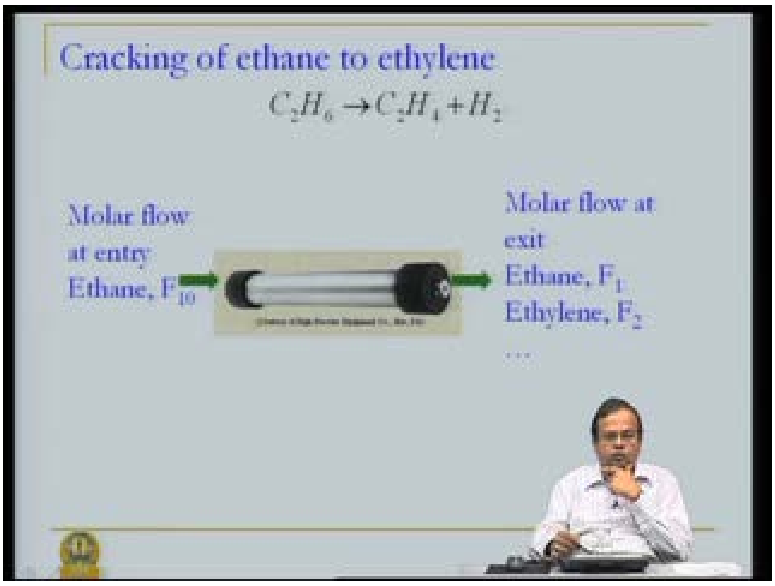

Cracking of ethane to ethylene

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Molar flow at entry
Ethane, F_{10}

Molar flow at exit
Ethane, F_1
Ethylene, F_2
...

So, this is all about basic representation of a reaction and monitoring of its conversion. Now, how do we use this information? So, let us go back to let us go back to our example of ethane or ethane cracking to ethylene. And let us say that we are doing these reactions in a tubular reactor. the real reactor does not look like this, but this is only schematic good enough for our purpose.

And let us say that there is certain flow in terms of moles that the gas is entering in the reactor. And there is a certain flow; it is coming out of the reactor at the exit of the reactor. So, one of the first steps in design equations that we saw at the first beginning of this class that we have to do is actually, you relate these flow rates in terms of either extent of reaction or conversion of reaction and so on.

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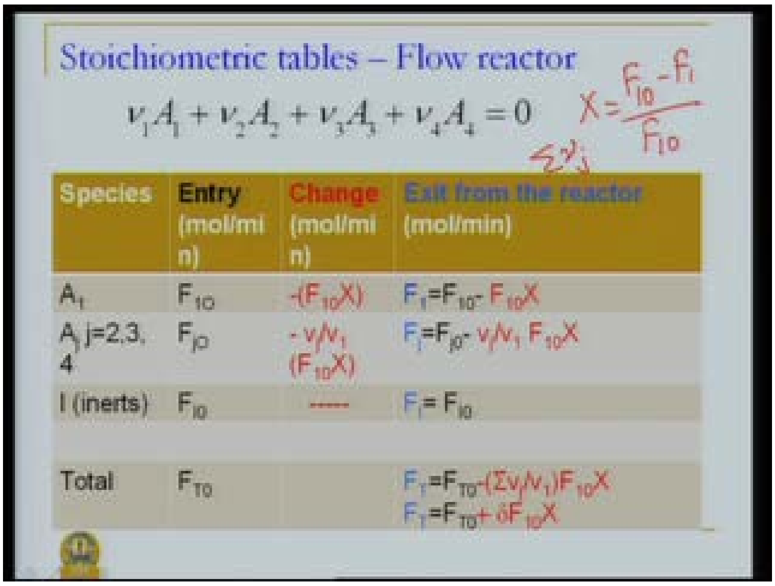

Stoichiometric tables – Flow reactor

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$X = \frac{F_{10} - F_1}{F_{10}}$

$\Sigma \nu_j$

Species	Entry (mol/min)	Change (mol/min)	Exit from the reactor (mol/min)
A_1	F_{10}	$-(F_{10}X)$	$F_1 = F_{10} - F_{10}X$
A_j j=2,3, 4	F_{j0}	$-\nu_j/\nu_1 (F_{10}X)$	$F_j = F_{j0} - \nu_j/\nu_1 F_{10}X$
I (inerts)	F_{I0}	-----	$F_I = F_{I0}$
Total	F_{T0}		$F_T = F_{T0} - (\Sigma\nu_j/\nu_1)F_{10}X$ $F_T = F_{T0} + \delta F_{10}X$

And the way we do that is by setting up the stoichiometric table and this is done in the following manner. It is a very systematic approach which is illustrated here, for with the reaction let us say involves four species. So, nu 1 A 1 plus nu 2 A 2 plus nu 3 A 3 plus nu 4 A 4 equal to 0 is my reaction.

I have a table here, first column is the species. Corresponding moles molar flow rate at the entry of the reactor. How much has changed in the reaction in the reactor rather. And what is at the exit of the exit of the reactor. For sake of simplicity, I am going to assume that my species A 1 is my limiting species and I am going to define my conversion of this species, in terms of the molar flow rates of this species A 1. Or in other words, I am going to define my conversion X as F 1 0 minus F 1 divided by F 1 0.

Let us quickly go through this table, it is just nothing but book keeping of what is happening in the reaction. So if I am looking at species A 1, then I have F 1 0 that is coming in, what has changed in the reactor is F 1 0 times X and what is coming out of the reactor, F 1 is F 1 0 minus F 1 0 into X.

For all other species, now I can write a corresponding molar flow rate in terms of this kea species and its conversion. So, let us say we are looking at any species j e j for which entry flow rate is F j 0, the change now will be recall that we have a stoichiometric to worry about. So if F 1 0 X moles of A 1 has change, then nu j divided by nu 1 times this F 1 0 into X is what species j has changed. So, the change in number of moles of j th species is nu j by nu 1 into F 1 0 X. It is true for all remaining species 2, 3, 4 and we have F j as F j 0 minus nu j by nu 1 into F 1 0 into X.

For sake of argument, and because for ethylene example, there was steam and steam is like an inert. If I have inert, coming in at a rate F 1 0, changed F 1 equal to F 1 0. That is, inert do not change. So, number of moles of inert coming in and going out are same, there is no change. Then we can sum up all these species and write what is the inlet flow rate? What is the outlet flow rate? and we write outlet flow rate in a compact form F T as total F T as F T 0, that is what is coming in plus this delta, which is this minus nu summation nu j by nu 1 into F 1 0 into X. So, this is my stoichiometric table. Where do I use this stoichiometric table?

Remember, we are dealing with, if we are dealing with gaseous reactions then there is a change in number of moles, as the reaction proceeds. For example, in the ethane example ethane to ethylene, starting with one reactant mole, we are getting 2 reactant moles of product. So, there is a change in number of moles. In fact, this summation nu j term will this term over here summation nu j will reflect that what is the change in number of moles?

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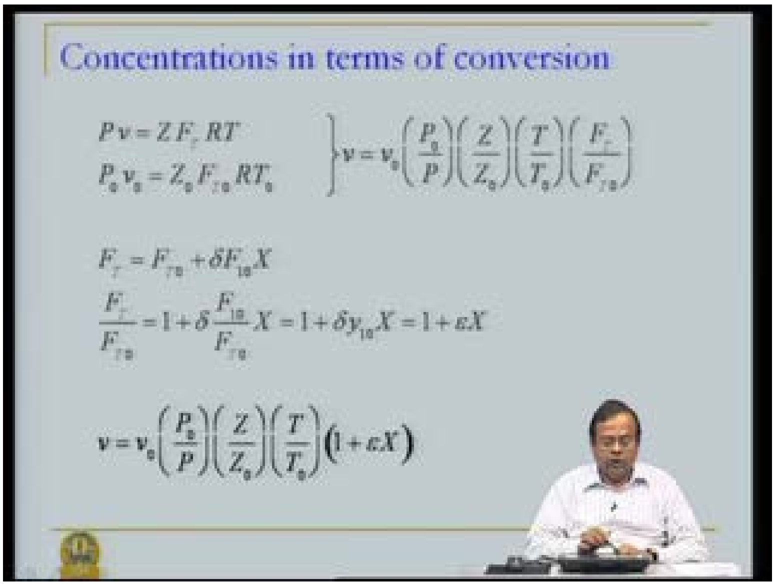

Concentrations in terms of conversion

$$\left.\begin{aligned} Pv &= ZF_T RT \\ P_0 v_0 &= Z_0 F_{T0} RT_0 \end{aligned}\right\} v = v_0\left(\frac{P_0}{P}\right)\left(\frac{Z}{Z_0}\right)\left(\frac{T}{T_0}\right)\left(\frac{F_T}{F_{T0}}\right)$$

$$F_T = F_{T0} + \delta F_{10} X$$

$$\frac{F_T}{F_{T0}} = 1 + \delta\frac{F_{10}}{F_{T0}}X = 1 + \delta y_{10} X = 1 + \varepsilon X$$

$$v = v_0\left(\frac{P_0}{P}\right)\left(\frac{Z}{Z_0}\right)\left(\frac{T}{T_0}\right)(1 + \varepsilon X)$$

So, if there is a change in number of moles. We have to now write for concentrations in terms of conversions. For a reaction in which there is a change in number of moles. Of course, concentration has to be written in terms of conversion, irrespective whether there is a change in number of moles. But some additional complexities arise, if there is a change in number of moles. And let us say that we use equation of state, P v equal to in this particular case for a flow reactor P v, v here denotes the volumetric flow rate is F T into R T, if it is an ideal law. There is, this is at the exit this is nothing but ideal gas law, if this factor compressibility factor Z is unity.

But in general equation of state, we can write P v equal to Z F R T at the exit of the reactor, at the entry of the reactor. So, subscript O denotes the entry. Notice now, I can combine these two equations and that will result into volumetric flow rate v, at the exit of the reactor is different from volumetric flow rate, at the entry of the reactor, because pressure, temperature, and flow rates are changing along the length of the reactor.

So, what we are essentially saying is suppose this is my entry point and I have reaction and exit point. Between entry point and exit point, my pressure may be changing, why? Because that could be pressure drop along the length of the reactor, my temperature may be changing, because there is associated heat factors or by molar flow rate may be changing, why? Because there is a change in number of moles. And as a result of all these factors, my flow rate of entry could be different than flow rate of exit. And I need to relate these quantities, so this is the first step in that in that direction.

Now, pressure and temperature to write to know, how pressure is changing along the length of the reactor, what do you need? You need momentum balance; we will come to that little later on. For knowing, how temperature is changing along the reactor, we need energy balance. What we have currently is only information about how flow rate is changing? Molar flow rate is changing between the entry and exit. And this is from that stoichiometric table earlier. So, we have inlet molar flow rate inlet molar flow rate and exit molar flow rate F T and F T 0, related to each other through this set of equation F T by F T 0. In its final form, we will get 1 plus epsilon X. So, this epsilon actually is nothing but this factor delta, we talked about earlier and this y 1 y 1 0.

So, if we put this two information together, we now get that is substitute for F T by F T 0 in this particular equation. We get volumetric flow rate changes along the length of the reactor in this particular manner.

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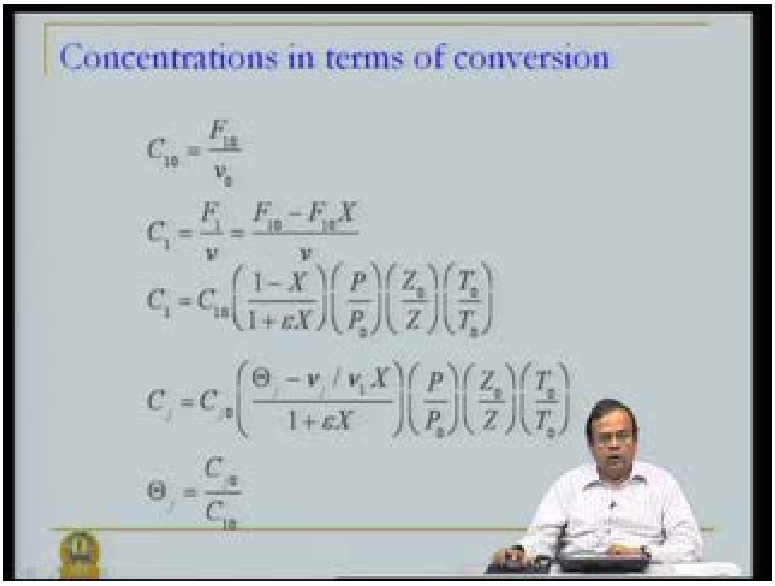

Concentrations in terms of conversion

$$C_{10} = \frac{F_{10}}{v_0}$$

$$C_1 = \frac{F_1}{v} = \frac{F_{10} - F_{10}X}{v}$$

$$C_1 = C_{10}\left(\frac{1-X}{1+\varepsilon X}\right)\left(\frac{P}{P_0}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{T_0}{T_0}\right)$$

$$C_j = C_{j0}\left(\frac{\Theta_j - v_j / v_1 X}{1+\varepsilon X}\right)\left(\frac{P}{P_0}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{T_0}{T_0}\right)$$

$$\Theta_j = \frac{C_{j0}}{C_{10}}$$

I will quickly wrap up our today's lecture by saying that this information, in term is related to the concentration changes. So, let us define the concentration at the inlet, as molar flow rate divided by volumetric flow rate. So, moles per liter, a moles per rather moles per minute divided by liters per minute giving rise to moles per liter.

Same thing at the exit, F 1 by v, where we know this F 1 is related in terms of conversion volumetric flow rate v. Now for v, we use the previous equation where we had this variation along the length of the reactor. If you put all this together, for my key species, concentration C 1 changes from its inlet concentration, which is dependent on the conversion, which is dependent on how pressure changes in the reactor, how temperature changes in the reactor. And similarly, we can write a similar equation for all remaining species 1, 2, 3, 4, 5 up to N, whatever species that are there and express concentration in terms of conversion.

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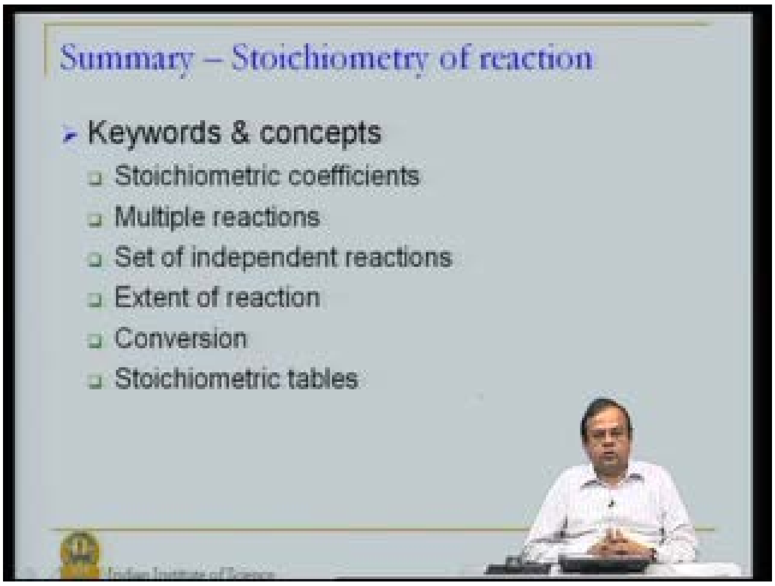

Summary – Stoichiometry of reaction

- Keywords & concepts
  - Stoichiometric coefficients
  - Multiple reactions
  - Set of independent reactions
  - Extent of reaction
  - Conversion
  - Stoichiometric tables

So now, let us summarize today’s class. What we saw today, was basically how to represent a reaction. we are just getting into our reaction engineering. So, the starting point naturally is how to express our reactions. Some of the keywords that you heard in today’s class are stoichiometric coefficient. Those numbers which tell you how many moles of Carbon monoxide reacts with how many moles of Hydrogen to give how many moles of methanol. we also talked about more than one reaction possible. So, multiple reactions, but when you have set of multiple reactions, we need not all reactions, but only independent reactions.

So, we have rank of the stoichiometric matrix telling us, what is the independent number of independent reactions. And then we defined two ways, in which we can monitor the progress of the reaction, namely extent of reaction and the conversion. And finally, how we put all these information together, to develop stoichiometric tables, so that we can eventually use them in our design equations.

So, this is as far as the strychometry is concerned. In the next class, we are now going to get into thermodynamics, because if you recall, I said conversion may not go to hundred percent for certain reactions certain reversible reactions. So our next lecture will be focused on, looking at reversible reactions and what information we get out of thermodynamic properties of a reacting system. Thank you.