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**Lecture No -32**

**Reactor Synthesis for Complex Reactions by Attainable Region: Fundamentals**

Welcome to module 7 of plant design and economics. In this module we are talking about reactor network synthesis. Now reactor network synthesis is essentially establishing the configuration of chemical reactors and establishing interconnections, among them. Reactor network synthesis for complex reactions is much more complex problem compared to synthesis for single reactions. In this module we will learn about a method known as attainable region.

Attainable region has a geometric flavor in it and will start with the fundamentals of attainable region today. In the next two lectures will learn more about attainable region method through examples.

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**Reactor Network Synthesis: Complex Reactions**

Given the complex reaction mechanism and kinetics, what is the optimum type and arrangement of the reactors that would maximize product yield?

$A \xrightleftharpoons[k_2]{k_1} B \xrightarrow{k_3} C, 2A \xrightarrow{k_4} D$  where:  $r_1 = k_1 C_A, r_2 = k_2 C_B, r_3 = k_3 C_B, r_4 = k_4 C_A^2$

The slide displays three reactor configurations: 1) CSTR followed by PFR; 2) PFR followed by CSTR; 3) CSTR followed by PFR. Below these, a sequence of three reactors (Reactor 1, Reactor 2, Reactor 3) is shown with interconnecting streams.

So today we will start with fundamentals of attainable region. So the kind of problem that you are talking about is as follows. Given the complex reaction mechanism and kinetics, what is the optimum type and arrangement of the reactors that would maximize product yield? So consider the given chemical reaction. A reversibly undergoes to B, which irreversibly undergoes to C and 2A goes to D, the rate expressions are given.

Now we can carry out this reaction in various configurations of chemical reactors. So what is the optimum type and arrangement of the reactors that would maximize the productivity, for example let us say I want to maximize the product of B. What should be my optimum reactor configurations.

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**Approach to reactor Network Synthesis**

The traditional way for reactor synthesis is to consider a large number of combinations of units, usually CSTRs or PFRs, and compute their performances for various designs.

This method is tedious and does not ensure that the best reactor has been found.

Two Approaches:

1. Attainable Region: Geometric Method
2. Optimization Method

The slide features a background with faint icons of a tree, a gear, and a reactor. A presenter is visible in the bottom right corner. Logos for IIT Bombay and NPTEL are in the bottom left.

The traditional way for reactor synthesis is to consider a large number of combinations of units. Let us say we will make use of CSTR and PFR for simplicity. So the traditional method will be to use a large number of combinations of CSTRs and PFR and compute their performance for various designs. Obviously this method is TDS. It takes lot of time and does not ensure that the best reactor network has been found.

So there are two approaches one is attainable region, which is a geometric method, another is optimization method where you formulate the reactor network synthesis problem as an optimization problem and solve the optimization problem to obtain the optimal reactant network. In this module, we will learn about attainable region.

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## AR: The Reactor Network Synthesis Problem

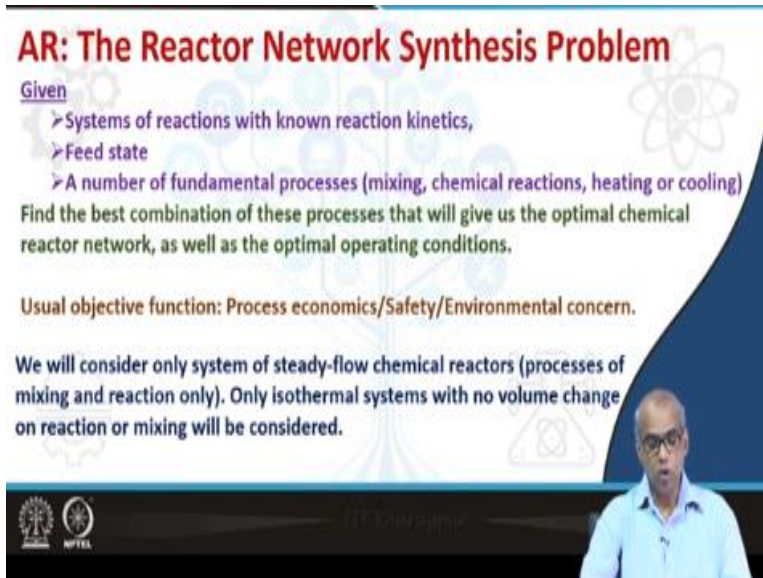
Given

- Systems of reactions with known reaction kinetics,
- Feed state
- A number of fundamental processes (mixing, chemical reactions, heating or cooling)

Find the best combination of these processes that will give us the optimal chemical reactor network, as well as the optimal operating conditions.

**Usual objective function: Process economics/Safety/Environmental concern.**

We will consider only system of steady-flow chemical reactors (processes of mixing and reaction only). Only isothermal systems with no volume change on reaction or mixing will be considered.



So let us refine the reactor network synthesis problem. Suppose we are given systems of reactions with known reaction kinetics, we are given the feed state and we are given a number of fundamental processes such as chemical reactions, mixing, heating or cooling. So we have been given units to perform these fundamental processes. For example CSTR PFR mixing, heating, cooling etcetera.

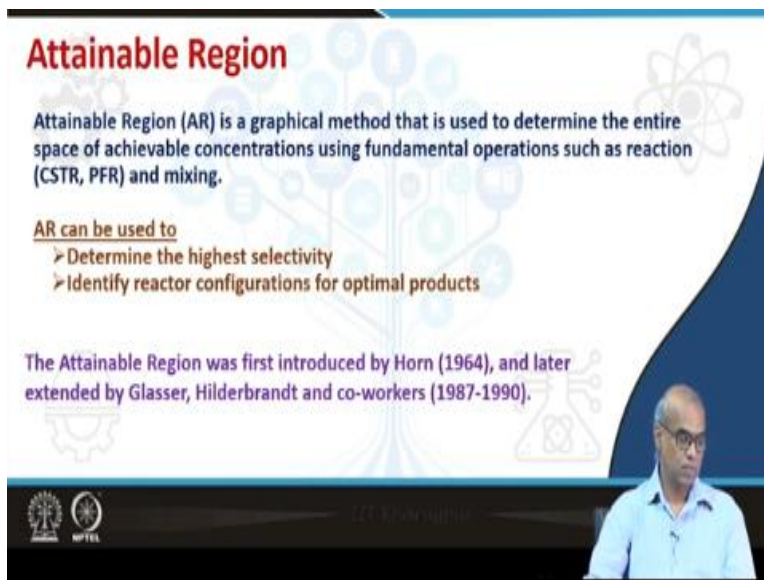
Now once these are given would like to know what is the best combination of these fundamental processes that will give us the optimal chemical reactor network, as well as the optimal operating conditions to achieve my target? So every optimization problem will have an objective functions. The target is your objective function which is frequently considered as process economics. But also safety concern, environmental concern can also be considered process objectives.

When you talk about attainable region will consider only system of steady flow chemical reactors. So process of mixing and reaction only. So we will talk about CSTR, PFR and mixing of streams. So, these are the three fundamental process we will consider to derive at an optimal reactor network through method of attainable region. And we are considering isothermal system with no volume change or reaction or mixing will be considered.

So, only isothermal systems with no volume change on reaction or mixing will be considered. Note that although we are considering here only continuous operations, we are making use of

only CSTR and PFRs but in the literature at enabled region has also been used to obtain batch chemical reactor networks. But for the purpose of this course will restrict ourselves to continuous processes, again we will also restrict ourselves to isothermal systems with no volume change on reaction or mixing.

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**Attainable Region**

Attainable Region (AR) is a graphical method that is used to determine the entire space of achievable concentrations using fundamental operations such as reaction (CSTR, PFR) and mixing.

AR can be used to

- > Determine the highest selectivity
- > Identify reactor configurations for optimal products

The Attainable Region was first introduced by Horn (1964), and later extended by Glasser, Hilderbrandt and co-workers (1987-1990).

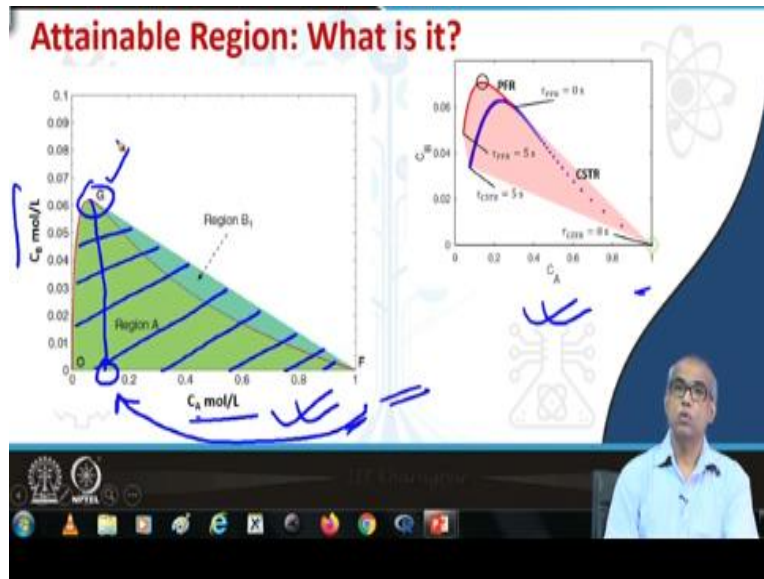
The slide features a background with faint chemical symbols and a network diagram. A speaker is visible in the bottom right corner of the slide frame.

Attainable region is a graphical method that is used to determine the entire space of achievable concentrations using fundamental operations such as reaction and mixing. So when a heat stream enters a reactor or a reactant network and from the other effluent from the reactor come up. So we are interested in the concentrations of the desired products in the effluent stream. The product distributions in the fluid stream the concentrations of the desired product in the effluent stream.

Attainable region is a graphical method that can be used to determine all the achievable concentrations. In the reactor effluent stream that can be obtained through chemical reactor networks and using fundamental operations such as CSTR, PFR and mixing. Attainable region can be used to determine the highest selectivity. It can be used to identify reactor configurations for optimal products.

The attainable region was first introduced by Horn in 1964 and later it was extended by Glasser Hilderbrandt and co-workers during 1987 to 90s. Even now also the research on attainable region is very active in literature.

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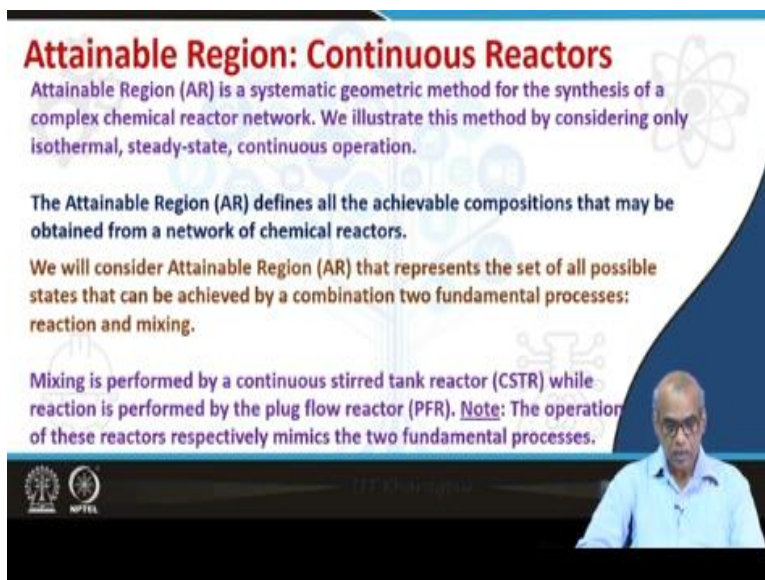
So what is attainable region? As we just discussed, it gives you the all achievable concentrations by fundamental operations using reactant networks. Now what you see in figure are examples of attainable region. So consider these entire region, entire color region either in this figure or this figure. Any point within this region represents a concentration. Note that these figures are plot of concentration of A versus concentration of B.

So we are considering a reaction let us say a complex reactions and we are interested in only concentration of A and concentration of B. So A and B are my important species for the chemical reactions. Let us say A is the feed and B is the desired product. Let us say there are other species such as C, D, E etcetera in the complex network, in the reaction network. But let us say the reaction mechanism is such that it is possible to express the concentration of B by looking at concentration of A alone.

So it is possible to make a plot of  $C_A$  versus  $C_B$  and obtain all the possible concentrations that are achievable through a reactor network see that can be achieved. Then we can find out my desired concentrations in the reactor effluent from such a figure using an objective function now. For example the point G corresponds to the maximum concentration of CB, maximum concentration of B.

And here their concentration is this. So this point corresponds to the concentration of A and B in the effluent of some reactor network. Note that we start with say 1 mole per liter of A and during reaction it has decrease to this value whereas B has increased to this value. Similarly each and every point on this region is achievable by some reactor network. So, attainable region method will allow us to find out those reactor networks.

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**Attainable Region: Continuous Reactors**

Attainable Region (AR) is a systematic geometric method for the synthesis of a complex chemical reactor network. We illustrate this method by considering only isothermal, steady-state, continuous operation.

The Attainable Region (AR) defines all the achievable compositions that may be obtained from a network of chemical reactors.

We will consider Attainable Region (AR) that represents the set of all possible states that can be achieved by a combination two fundamental processes: reaction and mixing.

Mixing is performed by a continuous stirred tank reactor (CSTR) while reaction is performed by the plug flow reactor (PFR). Note: The operation of these reactors respectively mimics the two fundamental processes.

The slide features a blue and white background with a molecular structure graphic. A video inset in the bottom right shows a man in a light blue shirt speaking. Logos for IIT Bombay and NPTEL are visible in the bottom left corner.

So, attainable region is a systematic geometric method for the synthesis of a complex chemical reactor network. Will illustrate this method by considering only isothermal steady state continuous operation, so make use of CSTR, PFR and also as fundamental process will be using mixing, mixing of streams. The Attainable region defines all the achievable compositions that may be obtained from a network of chemical reactors as we discussed in the previous slides.

We will consider attainable region that represents the set of all possible steps that can be achieved by combination of two fundamental processes reaction and mixing. Mixing is performed by a continuous start time reactor CSTR, while reaction is performed by the plug flow reactor. Note that CSTR and PFR stay at completely two ends when it talks about the mixing within the reactor.

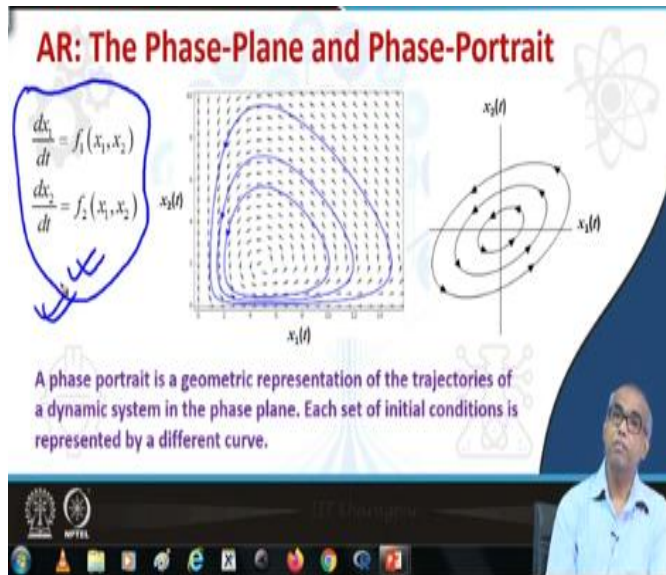
CSTR represents a reactor, which is completely mixed whereas the PFR there is no axial mixing. So the operation in this CSTR and PFR respectively mimics the two fundamental processes, such as mixing and reaction.

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So now we will look into some introductory elements that are necessary to understand and construct attainable region for chemical reactant networks.

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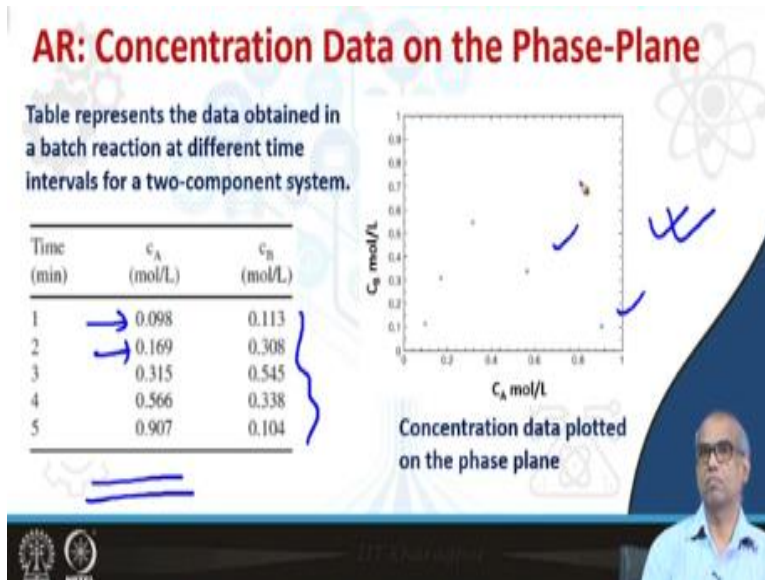


First the phase plane and phase portrait consider a system described by these two differential equations.  $\frac{dx_1}{dt} = f_1$ ,  $\frac{dx_2}{dt} = f_2$ ,  $f_1$  and  $f_2$  are both functions of  $x_1$  and  $x_2$ . Now with various initial conditions I can solve these two differential equations and then can mark a plot of

$x_1$  versus  $x_2$ . So the trajectories of  $x_1$  and  $x_2$  can be plotted and what I will get is a phase portrait on the phase plane of  $x_1, x_2$ .

So a phase-portrait is a geometric representation of the trajectories of a dynamic system in the phase plane. Each set of initial condition is represented by a different curve because you can solve these differential equations using various initial conditions and for each initial condition you will obtain a different curve.

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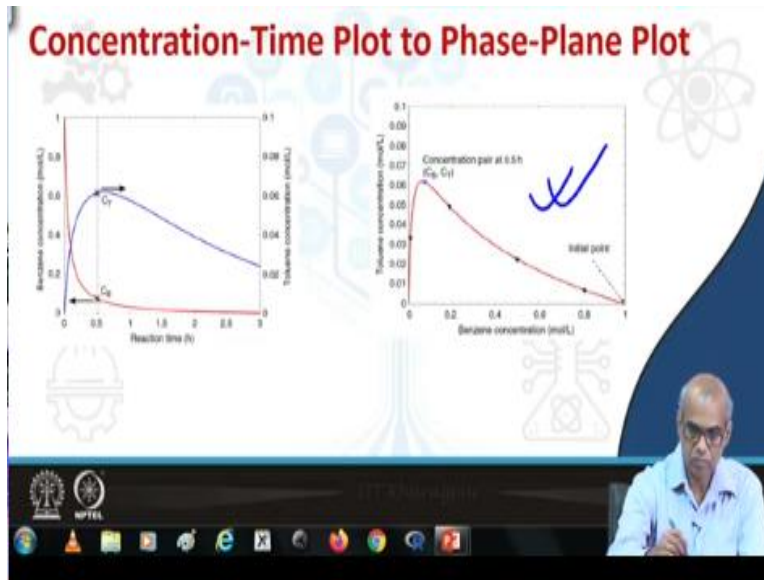


Now, let us consider a batch chemical reactor and let us consider that we are interested in two components concentration of A and concentration of B in the reactor. So I measure the concentration of A and concentration of B in the batch reactor at various time intervals. So this table gives you the data for concentration of A and concentration of B starting from minute 1 to 5. Now, I can make a plot of concentration of A and concentration of B on  $C_A, C_B$  diagram.

Note that these 5 points  $C_A, C_B$  are plotted using  $C_A, C_B$  axis. So you say the concentration data has been plotted on the phase plane. Note that we have done away with the time by making a plot of  $C_A$  versus  $C_B$ . So each point on the  $C_A, C_B$  plane represents a concentration in the reactor.

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This is another example consider the benzene toluene system. This figure shows you how the concentration of benzene changes with time and how the concentration of toluene changes with time. So as the reactant the concentration of benzene decreases with time and as the product concentration of toluene increases with time goes through maxima and again comes down. Now these time data concentration of benzene versus time and concentration of toluene versus time this can be plotted on concentration of benzene versus concentration of toluene.

So, this is the phase plane plot that I obtained from benzene toluene system from this concentration plot. For example, let us consider time 0.5 hour. So read the concentration of benzene and the concentration of toluene. So concentration of toluene is around 0.06, whereas concentration of benzene is quite small. This value may be even 0.05 around 0.05, so 0.05, 0.06, 0.05 around 0.05 or close to 0.01, 0.05, 0.06 something like that and 0.06 so obtain this point.

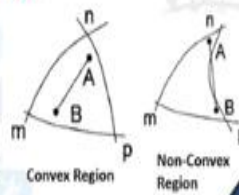
Similarly you obtain all other points and get this phase plane on concentration of benzene and concentration of toluene. So we will make use of such phase plane for construction of attainable region.

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## Attainable Region: Convex Region

Attainable Region has the property of convexity.

Take any two points A and B in a region. The region is convex if all the points of the segment A-B lies within the region. In other words, in a convex region all the vectors point-out into the region, or they are tangent at most to its boundary, or zero.



The Convex Hull of a set of points is defined as the smallest convex polygon, that encloses all of the points in the set. The polygon has no corner that is bent inwards. A concave region can be transformed into a convex one by adding a Convex Hull.



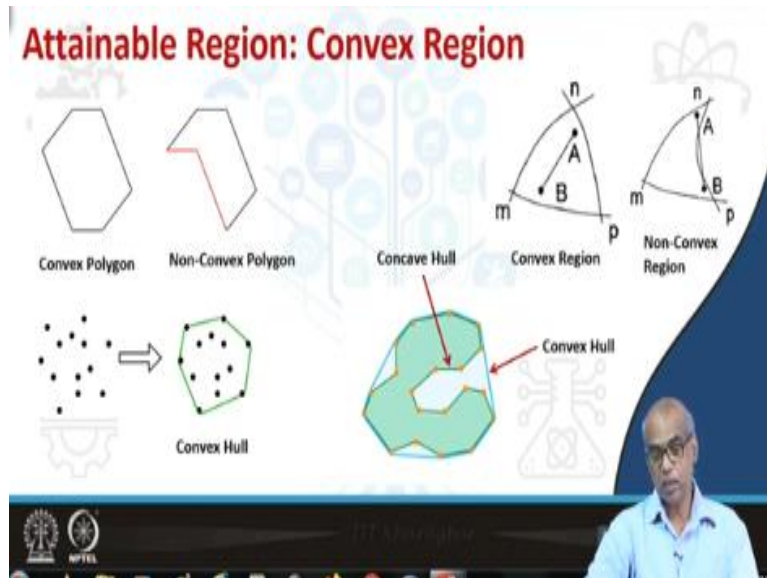
Now there is an interesting property of attainable region, attainable region has to be convex. So, attainable region has the property of convexity. Take any two points A and B in a region. The region will be convex if the line segment A B lies completely within the region. So a convex region is defined as follows. You take any two points within the region join these two points by line segment it if every point on this line segment lies completely within the region this is convex region.

Otherwise it is non convex region, concave region. Note that this is convex region, whereas this is not convex because when I join A and B by the line segment there are several points on the line, which lies outside the region. In a converse region all the vectors point out into the region or there tangent at most to its boundary or 0. So when you have a convex region all the vectors point out into the region or they tangent at most to its boundary or 0.

This will make use later when you discuss more about the attainable region. Let us now define convex hull. The convex hull of a set of points is defined as the smallest convex polygon that encloses all of the points in the set. So the convex hull of a set of points is defined as the smallest convex polygon that encloses all of the points in the set. The polygon has no corner that is bent inwards.

A concave region can be transformed into a convex 1 by adding a convex hull. So it is possible to convert a concave region into a convex region by adding a convex hull.

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So, let us see how we do that. What do you see is example of convex polygon and non convex polygon. Now you consider these sets and here look at the polygon constructed by the green line. So these polygon represents the smallest polygon and the smallest convex polygon that encloses all the points. So, this is the convex hull. Another example of convex hull so; this polygon represented by this blue line is the convex hull.

Whereas the polygon represented by this green line is not a convex hull, it represents a concave hull. But note that the convex hull the concave polygon has been converted to a convex polygon by putting a convex hull around it.

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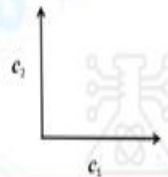
## AR: The Concentration Vector

Consider that we have a set containing  $N$  species with molar concentrations  $c_1, c_2, \dots, c_N$ . These concentrations can be represented by a vector containing  $N$  component concentrations.

$$C = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} \text{ or } C = [c_1 \ c_2 \ \dots \ c_N]^T$$

These concentrations may be a result of mixing pure components and/or reactions between them.

Thus,  $C$  represents a unique coordinate in concentration space that may indicate the instantaneous concentration within a reactor, or the resulting composition formed from a combination of mixing many effluent streams.



Next will define a term concentration vector, consider that you have a set containing  $N$  species with molar concentration  $c_1, c_2$  up to  $c_n$ . These concentrations can be represented by vector containing  $n$  component concentrations. So we can represent the concentration vector as the column vector which contains concentrations of all the species in your reactor. These concentrations may be a result of mixing pure components or reactions between them.

So in two dimensions I can make a plot  $C$  represents a unique coordinate in concentration space that may indicate the instantaneous concentrations within a reactor or the resulting composition form from a combination of mixing many effluent streams. So in two dimensions, you can make a plot of  $C_1$  versus  $C_2$  and any point within this  $C_1, C_2$  plot will represent a concentration vector.

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### AR: The Concentration Vector

A mixture can be represented by a vector where the elements of the vector correspond to species concentrations of the mixture.

Multiple mixtures can be represented as vectors from the origin  $[0, 0]^T$  in concentration space.

Since each mixture is represented as a vector, each is associated with a unique magnitude and direction.

$$C_1 = \begin{bmatrix} 0.085 \\ 0.178 \end{bmatrix} \text{ mol/L} \quad C_2 = \begin{bmatrix} 0.171 \\ 0.178 \end{bmatrix} \text{ mol/L} \quad C_3 = \begin{bmatrix} 0.171 \\ 0.357 \end{bmatrix} \text{ mol/L} \quad \|C_1\| = \sqrt{0.085^2 + 0.178^2} = 0.197 \text{ mol/L}$$

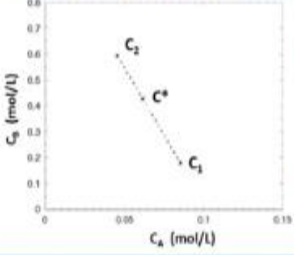
A mixture can be represented by a vector where the elements of the vector correspond to the species concentrations of the mixture. So look at this CA, CB plot we have represented C1, C2, C3 etcetera as different vectors and each vectors represents a mixture. For example, C1 is this vector and what are the components of the vector? CA and CB. So, this is CA and this is CB, similarly C2, similarly C3.

Multiple mixtures can be represented as vectors from the origin in concentration space that is what we have done in the figure. Since each mixer is represented as a vector each is associated with a unique magnitude and direction. You can find out the direction, you can find out the magnitude of the vector as shown for vector C1.

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### Attainable Region: Mixing Process: Lever Arm Rule

When density is assumed constant, mixing has a special geometric property. Mixtures lie on a straight line joining the two concentrations being mixed in concentration space. Mixing is therefore a linear process.




$$C^* = \lambda C_2 + (1 - \lambda) C_1 \quad 0 \leq \lambda \leq 1$$

$$\Rightarrow C^* = C_1 + \lambda(C_2 - C_1)$$

$C^*$  is a linear combination of  $C_2$  and  $C_1$ , and mixing is a linear process.

Generalization for  $k$  compositions:

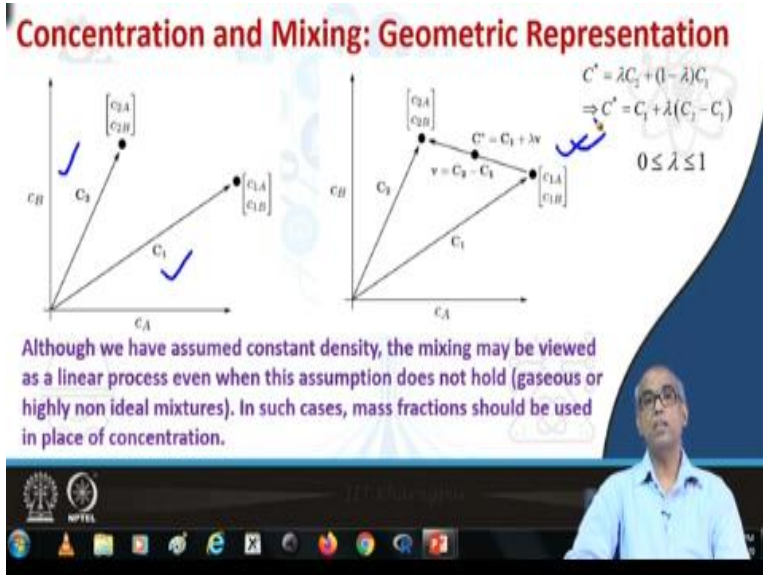
$$C^* = \sum_{i=1}^k \lambda_i C_i \quad \sum_{i=1}^k \lambda_i = 1$$


Now let us see how we represent mixing geometrically when density is assumed constant mixing as a special geometric property. Mixtures lie on a straight line joining the two concentrations being mixed in concentration space. Mixing is therefore a linear process. If you look at the figure the concentration plots  $C_1$  and  $C_2$  represent 2 mixtures. So  $C_1$ ,  $C_2$  are 2 vectors representing concentrations.

Now if I mix them I may get siesta and siesta will be obtained as a linear combinations of  $C_1$  and  $C_2$ . So siesta is obtained as a linear combination of  $C_1$  and  $C_2$ . So siesta equal to  $\lambda C_2 + 1 - \lambda C_1$ , where  $\lambda$  is values between 0 and 1. This we can extend for any number of compositions on necessary 2. Graphically, it is easier to represent 2 compositions. But for any number of  $k$  compositions this relation will hold.

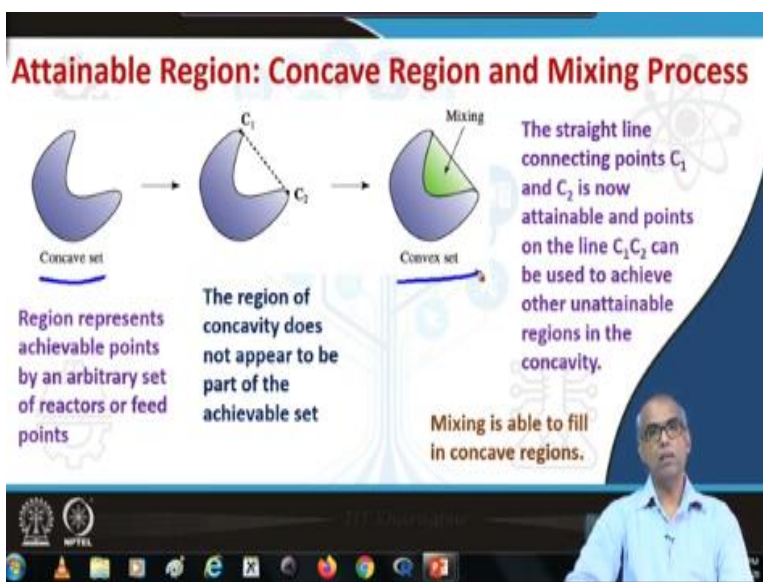
That the mixtures when you add say  $C_1$ ,  $C_2$ ,  $C_3$  upto  $C_k$  the resulting mixtures will be linear combinations of this  $C_1$ ,  $C_2$ ,  $C_3$  up to  $C_k$  as shown in this figure equation. Here again  $\lambda_1$ ,  $\lambda_2$  up to  $\lambda_k$  must be equal to 1.

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This figure again shows geometrically the concentrations and mixing. So you have two vector  $C_1$  and  $C_2$  representing concentrations. So mixtures now when you add them you get siesta. Although we have assumed constant density, the mixing may be viewed as a linear process even when this assumption does not hold. For example gaseous mixture, or highly non-ideal mixtures, however in such cases we can replace the concentration by mass fraction.

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Now consider this figures this is a concave set. This region represents let us say achievable points by an arbitrary set of reactors or feed points. So these concave set let us say it is represents achievable points by an arbitrary set of reactors or feed points. So, apparently it does not seem to be possible that will be able to obtain the concentrations lying within the concave region.

So the region of concavity does not appear to be part of the achievable set. But when you add C1 and C2 that means when you mix this two points C1 and C2, the straight line connecting point C1 and C2 is now attainable and points on the line C1 C2 can be used to achieve other attainable region in the concavity. So when you add C1 and C2, it will fill in the concave region. So from the concave set here, I obtain the convex set through mixing.

So mixing is able to fill in concave regions and what initially appeared to be not achievable now becomes achievable. So mixing expands the region the concave region can be converted to a convex region.

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**Attainable Region: Mixing Process: Important Results**

Given a convex set of points, there are infinitely many ways in which to achieve points within the region. Interior points can be obtained as intersection of many states that all cross at the same point. There is generally no unique combination of boundary points that can be used to achieve points located within the region.

This suggests that one need only be concerned with the boundary points of the AR, as all other points within the region may be attainable by mixing. The AR must therefore also be convex, formed from the Convex Hull of its boundary points.

The slide features a graph with the x-axis labeled  $c_a$  (mol/L) ranging from 0 to 1.0 and the y-axis labeled  $c_b$  (mol/L) ranging from 0 to 0.3. A green shaded region represents the attainable region, bounded by a concave curve. Points  $x_1$ ,  $x_2$ , and  $x_3$  are marked on the boundary. A dashed line connects  $x_1$  and  $x_2$ , passing through  $x_3$ . A speaker is visible in the bottom right corner of the slide.

This leads to an important result given a convex set of points there are infinitely many ways in which to achieve points within the region. Interior points can be obtained as intersection of many states that all cross at the same point. There is generally no unique combination of boundary points that can be used to achieve points located within the region. So, what do you mean is let us consider point  $x_1$ ,  $x_2$  and  $x_3$ .

Now point  $x_3$  can be obtained by linear combinations of point  $x_1$  and  $x_2$ ,  $x_3$  can also be obtained by let us say point  $x_4$  and point  $x_5$  by linear combinations of point  $x_4$  and  $x_5$ . So we can consider several such mixing where the line passes through  $x_3$ ,  $x_3$  is a point within the region.



So there may be various combinations of points on the boundary of the region which when added will get a point within the region.

So this leads to an important conclusion that one is only concerned with the boundary points of the attainable region. As all other points within the region may be attained by mixing attainable region must therefore also be convex formed from the convex hull of its boundary points.

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**AR: The Reaction Rate Vector**

We have defined a mixture concentration compactly as a vector of species concentrations. Similarly, it is also possible to form a vector associated with the rate of reaction.

Consider:  $A \xrightarrow{k_1} B \xrightarrow{k_2} D$  and  $A \xrightarrow{k_3} E$ . If A and B are the components of interest to the problem, the concentration vector is  $C = \begin{bmatrix} C_A \\ C_B \end{bmatrix}$

It is natural to express the corresponding rates of reaction for A and B as a two-component column vector. The Rate Vector,  $r(C)$ , in  $C_A - C_B$  space is defined as:

$r(C) = \begin{bmatrix} r_A(C) \\ r_B(C) \end{bmatrix}$

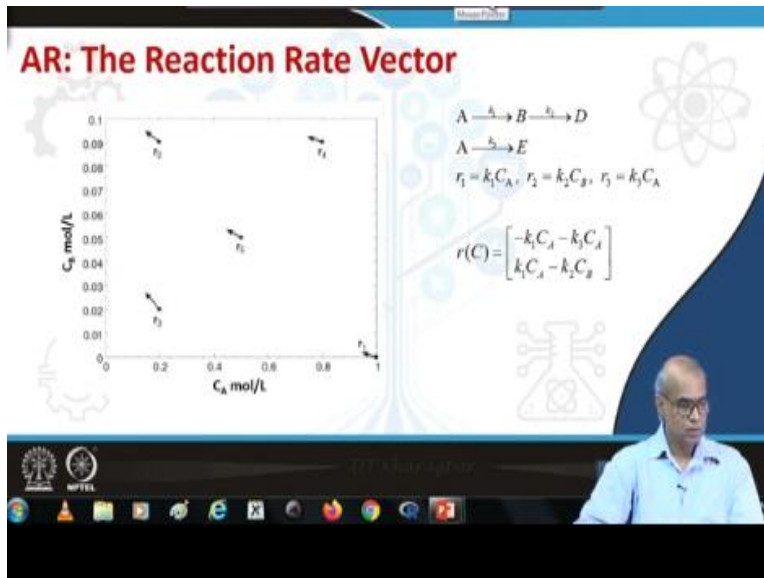
$A \xrightarrow{k_1} B \xrightarrow{k_2} D$   
 $A \xrightarrow{k_3} E$   
 $r_1 = k_1 C_A, r_2 = k_2 C_B, r_3 = k_3 C_A$

$r(C) = \begin{bmatrix} -k_1 C_A - k_2 C_B \\ k_1 C_A - k_3 C_A \end{bmatrix}$

Next we will define one more term known as reaction rate vector. We have defined a mixture concentration compactly as a vector of species concentrations. Similarly it is also possible to form a vector associated with the rate of reaction. Let us consider this reaction A to B to D and A to E. If A and B are the components of interest to the problem then the concentration vector is of course is a vector with two components CA and CB.

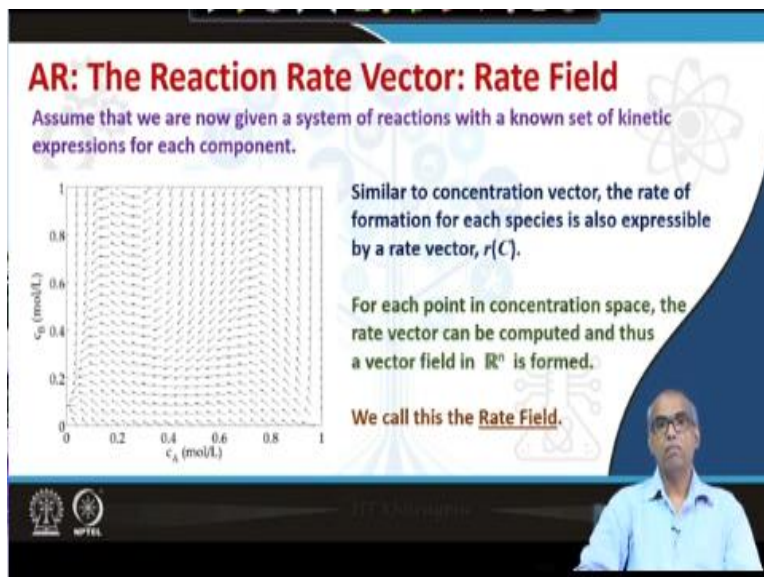
It is natural to express the corresponding rates of reactions for A and B as the two component column vector, will call that vector as rate vector. So rate of reaction for A and for B so the rate vector in C.A, CB space will be a 2 dimensional vector with components rate of reaction rA and rB. For example for this reaction if these are the rate constants given, rate expressions given we can find rA and rB and can put it here and we get the reaction vector, reaction rate vector.

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So this figure shows the reaction rate vectors. So, several rate vectors have been shown on the concentration space. So, all can be obtained from such expression for the rate vector. So, you must know the reaction rate expressions for the chemical reaction at hand.

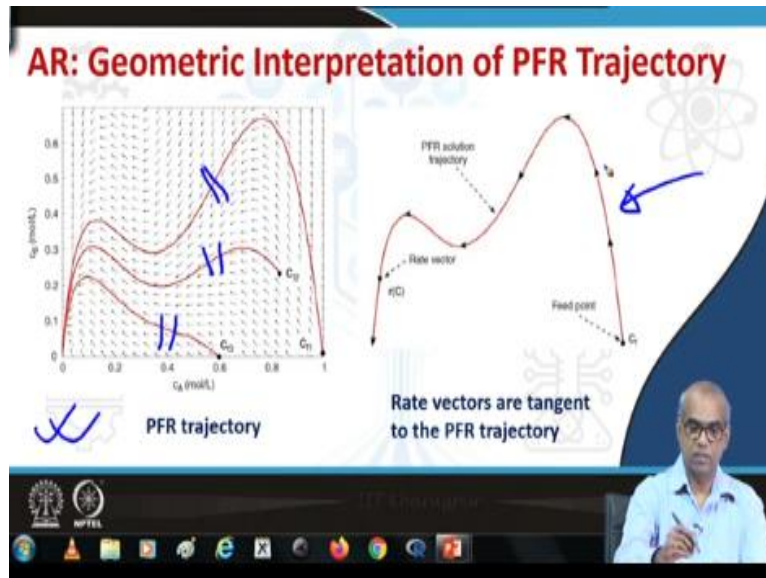
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Now, let us assume that we are now given a system of reactions with a known set of kinetic expressions for each component. Similar to concentration vector the rate of formation for each species is also expressible by rate vector and that is what we are seen in the previous slides. For each point in the concentration space the rate vector can be computed and thus a vector field is formed we call these the rate field.

Note in the figure in the concentration space, we have shown all the rate vectors and these constitute a vector field and we call this a rate field.

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This figure shows you a PFR trajectory interest, several PFR trajectories are shown. Starting from different initial concentration of the feed and the rate vectors are also shown. If we focus your attention on only one particular trajectory, the rate vectors are seen to be tangent to the PFR trajectory. This is another important interesting property the rate vectors are tangent to the PFR trajectory.

With this we will discuss our discussions on attainable region here and we will continue with this discussion in the next class.