Mathematical Modelling and Simulation of Chemical Engineering Process

Doctor Sourav Mondal
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture 01

Introduction

Hello and welcome to this course on Mathematical Modelling and Simulation of Chemical Engineering Process. As you know, chemical engineering involves a lot of processes at different scales involving different physics with different time dependent systems whether it is dynamic or steady state. So, the entire course is dedicated towards different and how we can model these sort of different processes, what is the modelling approach, how can we solve these models, how the models could be useful in industrial context and so many different mathematical approaches that is necessary for modelling complex to real life system.

Now, with this I would like to start the first introductory lecture on this course. And as you know since the course involves topics from different subject areas involving mass transfer, fluid flow, heat transfer, thermodynamics to some extent on this process instrumentation and control systems. The first couple of introductory lectures would be involved to review of those ideas, those concepts and try to gain more insight into the assumptions behind such physical systems or physical theories and to relate them to the actual context.

Now, as you can see in this course, the course is outlined to tell you about a variety of different processes ranging from mass transfer to chemical reaction engineering to separation processes. As I already said that these introductory lectures would be related to review of those important concepts which I am sure all of you must have gone through in your undergraduate course. So, we will try to look more into the details of it and try to understand that how these equations or how the mathematical framework actually evolves from understanding of these systems or the background concepts.

(Refer Slide Time: 03:24)

CONCEPTS COVERED

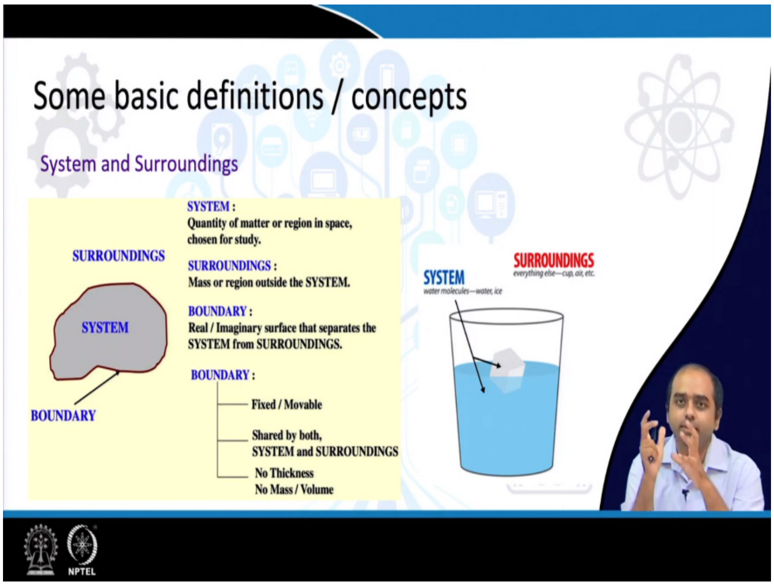
❑ Classification of systems – open and closed, steady and dynamic, distributed and lumped parameter systems

❑ Modelling approaches – deterministic versus stochastic

Now, with this I would like to start today's lecture and the first important topic that I would like to enlighten all of you in this today's lecture is about that how do we classify different systems. Now, when we call something as a system, it is very important to understand that the systems are also of different types.

So, how do we classify is one thing and the other thing is the approach and how do you model a certain system, whether it is a deterministic system, whether it is a stochastic system. I am going to talk about them towards the end of these introductory lectures. But before that, let us first focus on the classification of the systems of a variety of types.

(Refer Slide Time: 03:54)



Some basic definitions / concepts

System and Surroundings

SYSTEM :
Quantity of matter or region in space, chosen for study.

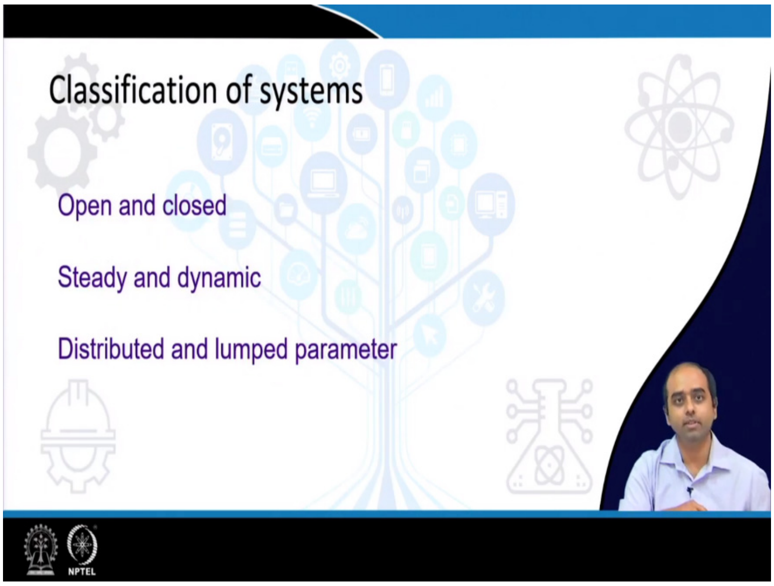
SURROUNDINGS :
Mass or region outside the SYSTEM.

BOUNDARY :
Real / Imaginary surface that separates the SYSTEM from SURROUNDINGS.

BOUNDARY :
- Fixed / Movable
- Shared by both, SYSTEM and SURROUNDINGS
- No Thickness
  No Mass / Volume

We define a system as a domain or the system domain is defined or segregated from the universe or let us say from the surroundings with the help of a boundary. So, this is a very important thing that I would like to highlight here that generally the presence of a boundary helps in identification of the system. So, the boundary could be fixed, it could be moveable, it may be imaginary distinction, it could be a real segregation of the system and the surroundings. But please note that it is the boundary which identifies the system.

(Refer Slide Time: 04:46)



Classification of systems

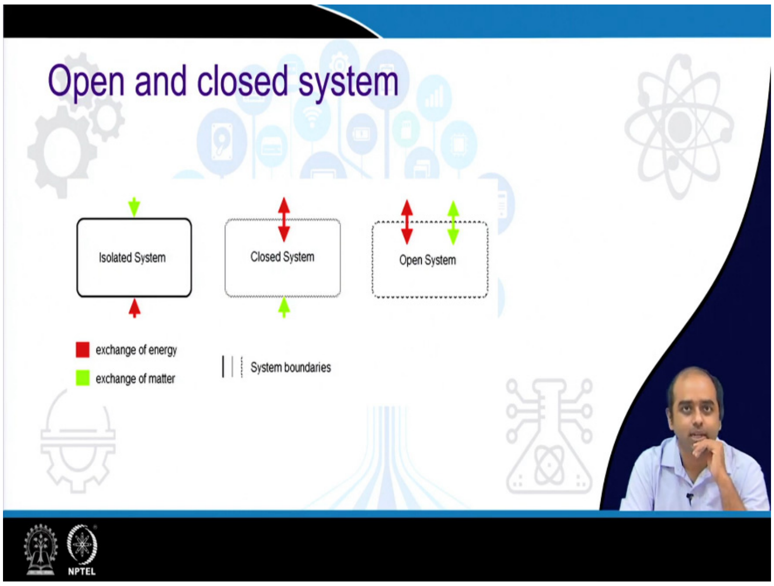
Open and closed

Steady and dynamic

Distributed and lumped parameter

So, now coming to the classifications of the different types of the system. As you know, systems could be a variety of types open and closed, steady and dynamic processes and it could be distributed or lumped parameter systems.

(Refer Slide Time: 04:58)



Open and closed system

Isolated System

Closed System

Open System

🟥 exchange of energy

🟩 exchange of matter

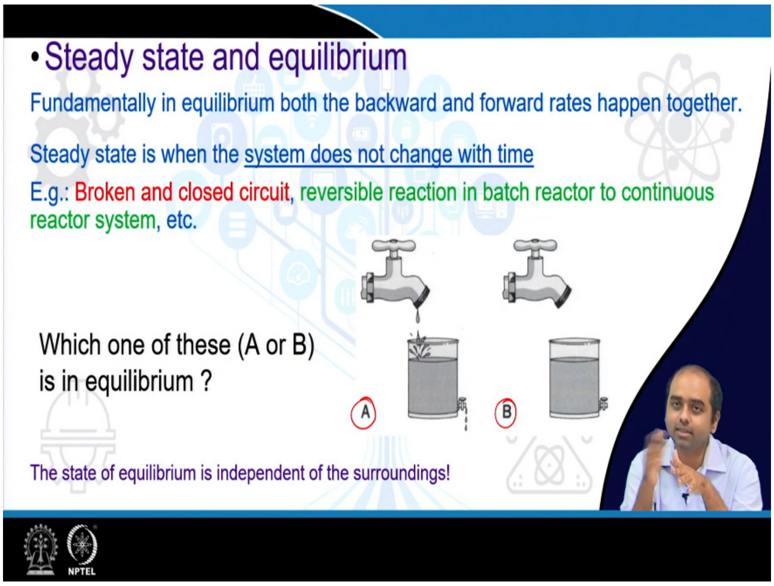
| ¦ System boundaries

Now, first coming to the open and the first category. Categorization of this process, open and the closed system, there are generally three types the isolated system, the closed systems and entirely open systems. And the boundary as you can see from this simple cartoon that the boundary actually make this distinction.

Now, in the case of the isolated system you have hard boundaries and neither meter nor mass or energy could get exchanged through this system. That is what we define as isolated system. Coming to the closed system and the distinction of the open system. In the case of closed systems, you can say that there is exchange of energy but there is no exchange of mass. And in the open system, the boundary, across the system boundary you can have exchange of both mass and energy. So, this is how these three types of systems are generally categorized.

So, isolated system could be sort of you can think of a box or having hard solid walls and the box is adiabatic. So, there is no exchange of energy or matter. In the case of closed system, you can think of a process where the same box but you do not have adiabatic walls. So, there is constant interaction with the energy. And in the case of open systems, you generally consider a small region of a big part and where there is continuous exchange of both mass and energy, the walls could be porous or permeable or you can consider the system to be a small part of a big domain. So, this is the importance of the boundary.

(Refer Slide Time: 06:46)



- Steady state and equilibrium

Fundamentally in equilibrium both the backward and forward rates happen together.

Steady state is when the system does not change with time

E.g.: Broken and closed circuit, reversible reaction in batch reactor to continuous reactor system, etc.

Which one of these (A or B) is in equilibrium ?

The state of equilibrium is independent of the surroundings!

Now moving ahead. How do we distinguish between a steady state and equilibrium? A steady state, as you all know, in both the cases, the steady state and the equilibrium case, the change in the system variable is not there or the rate of change of the system variable is constant. So, whether you are having a steady state or an equilibrium and the system dynamics does not change but there are some important differences in the case of the steady state and the equilibrium.

So, all of us have encountered this idea of equilibrium in the case of this reversible chemical reaction where we say that the backward and the forward rates are almost at equal rates and that is why there is no net change in the concentration.

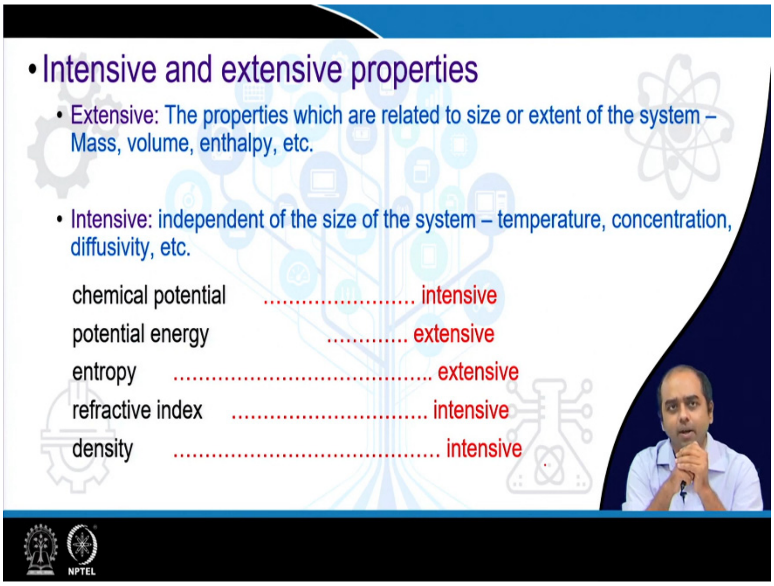
Now, other examples could be broken and closed circuits. So, in the case of the broken circuit, the system is in equilibrium because the potential difference is 0. Hence there is no charge transfer whereas in the case of the closed circuit, the charge transfer is at a steady state, right. So, in both these cases, you do not see there is no change in the system dynamics but essentially, there are differences.

I would also like to point out this simple case. I mean the first one and this first picture that you see here as denoted as A and this B. In both the case, the level of the water does not change, but both of them are not at the same state. How do we classify which one is at steady state and which one is at equilibrium?

So, you can see in the first state there is a constant input of water and there is a constant outlet. So, the water does not change. In the second case, there is no inlet, no outlet. So, the second case is definitely a case of the equilibrium, because the system does not interact with itself or with the surroundings. That is an important criterion for the equilibrium, because you can also say in this case that in the case of the equilibrium, the reactants, products or the necessary energy or the evolved energy are contained within an isolated system. So, that is very important to understand for the case of the equilibrium and the net change of the chemical potential or you have the free energy or the thermodynamic potentials all are equal to 0. And that is why essentially equilibrium exists whether you call it thermodynamic equilibrium, chemical equilibrium, mechanical equilibrium, this is the reason for the existence of the equilibrium.

So, the second case is about a scenario. This case B is a scenario of the equilibrium and this case A is definitely a case of steady state as well as here, you see there are two constant rates happening, the rate of filling and the rate of outlet of the water both are happening at the constant rate and leading to equilibrium in the state of the water level. So, in the case A you are achieving both equilibrium and steady state. Whereas in case B, it is only the case, it is only the situation of the equilibrium. So, please note that in the steady state, there is always an entropy change, right whereas in equilibrium, the entropy change is 0.

(Refer Slide Time: 10:24)

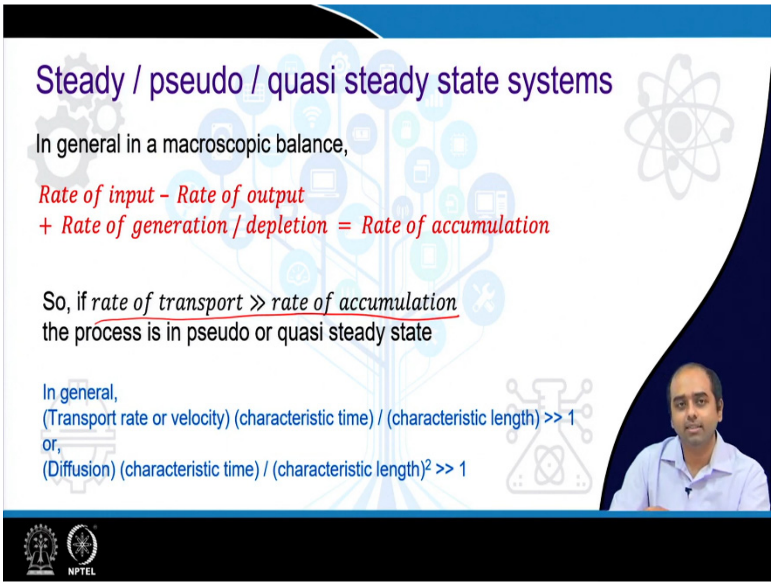


- Intensive and extensive properties
  - Extensive: The properties which are related to size or extent of the system – Mass, volume, enthalpy, etc.
  - Intensive: independent of the size of the system – temperature, concentration, diffusivity, etc.

chemical potential .... intensive
potential energy .... extensive
entropy .... extensive
refractive index .... intensive
density .... intensive

Moving ahead, these are some of the thermodynamic concepts, just to give you a quick brush up. Intensive and extensive properties. Something which depends or is related to the mass is known as extensive property. And something which is independent of the size of the system is generally known as the intensive property. So, examples of extensive properties are mass, volume, enthalpies and intensive properties are refractive index, density, chemical potential.

(Refer Slide Time: 10:57)



Steady / pseudo / quasi steady state systems

In general in a macroscopic balance,

Rate of input – Rate of output
+ Rate of generation / depletion = Rate of accumulation

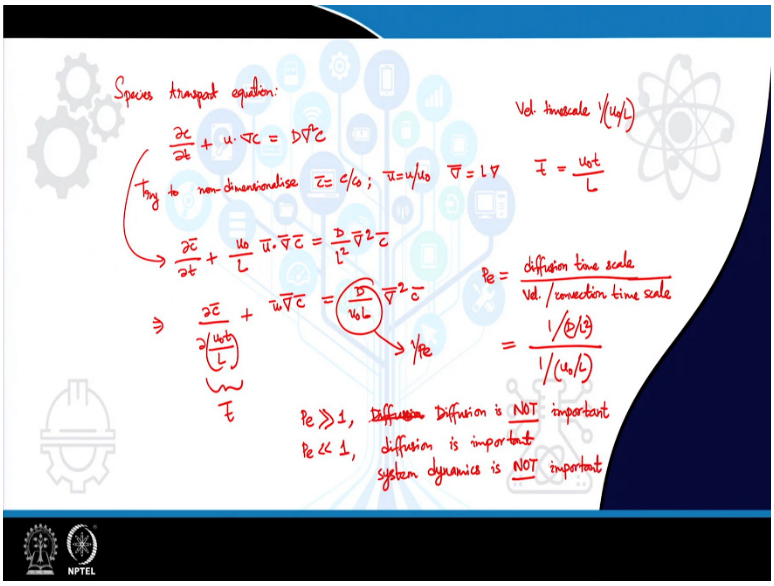
So, if *rate of transport* ≫ *rate of accumulation*
the process is in pseudo or quasi steady state

In general,
(Transport rate or velocity) (characteristic time) / (characteristic length) >> 1
or,
(Diffusion) (characteristic time) / (characteristic length)^2 >> 1

Now, the question comes that how do we define a steady and a quasi-steady system. I mean, what is the differentiation between a steady and a quasi-steady system? In steady state system, the dynamics or the rate of change of the process variable is equal to 0. But it may not be the case in quasi steady systems where we lead to an approximation. So, in general, what is the approximation? So, if we talk about a general process if the rate of transport is much much greater than the rate of accumulation, then we call that process to be in steady state.

Whereas on the other hand, if the accumulation rate is larger than the system is in a dynamic state but at steady state, the rate of transport is essentially 0. But it may not be always the case. It may be the rate of accumulation very small compared to the transport rate leading to a situation which we call is at the pseudo or the quasi steady state. So, in general, let us say for a diffusion system we can say that the diffusivity and the product of the diffusivity with the characteristic time and length scale squared, this ratio, if it is much much greater than 1, will lead to the condition that it is a quasi-steady or a pseudo steady state system.

(Refer Slide Time: 12:24)



Species transport equation:

$$\frac{\partial c}{\partial t} + u\cdot\nabla c = D\nabla^2 c$$

Try to non-dimensionalise $\bar{c} = c/c_0$; $\bar{u} = u/u_0$ $\bar{\nabla} = L\nabla$ $\bar{t} = \frac{u_0 t}{L}$

Vel. timescale $1/(u_0/L)$

$$\frac{\partial \bar{c}}{\partial t} + \frac{u_0}{L}\bar{u}\cdot\bar{\nabla}\bar{c} = \frac{D}{L^2}\bar{\nabla}^2\bar{c}$$

$$\Rightarrow \frac{\partial \bar{c}}{\underbrace{\partial\left(\frac{u_0 t}{L}\right)}_{\bar{t}}} + \bar{u}\bar{\nabla}\bar{c} = \boxed{\frac{D}{u_0 L}}\bar{\nabla}^2\bar{c} \quad \rightarrow 1/Pe$$

$$Pe = \frac{\text{diffusion time scale}}{\text{Vel. / convection time scale}} = \frac{1/(D/L^2)}{1/(u_0/L)}$$

$Pe \gg 1$, ~~Diffusion~~ Diffusion is NOT important

$Pe \ll 1$, diffusion is important

system dynamics is NOT important

Now, how do we come to this? Let us just do a quick analysis on this. So, let me try to help you with the species transport equation. So, this is something all of you are aware of. Let us say we try to non-dimensionalize the equation using the following scaling: I write c bar is equal to c by c naught. u bar is equal to u by u naught and this grad bar is equal to L grad, we define the time scale in terms of the velocity scaling as velocity time scale.

So, the velocity time scale can be defined as 1 by u naught by L. So, this equation now gets converted to (refer to the screen shot) in this form. This is just substitution of the scaling arguments and this further can be simplified or rewritten in this form. So, this is you can call this as the time scale of this problem. And all of you can identify that this quantity is 1 by the peclet number.

So, what is a peclet number? We all of us know that the peclet number is the ratio of the convection to diffusion. There is also another way to define it as the ratio of the diffusion timescale to the velocity or the convection time scale. So, in this case, the diffusion time scale is 1 by D by L square and the velocity time scale is 1 by u naught upon L.

So, you can clearly see that if peclet number is much much greater than 1, then diffusion to the problem, diffusion is not important, and the system is entirely dominated by the convection transport. If peclet number is much much less than 1, then diffusion is important, as well as you can observe that the system dynamics is not important and the system can be considered to be in a pseudo steady state provided you scale the system dynamics with respect to the velocity. So, if you are following a velocity time scale to the system and you find that the peclet number is much much smaller than one, you can interpret that the system is at a pseudo steady state condition.

(Refer Slide Time: 16:41)


Strategies for modelling a process.

1. Process → transient / SS // equilibrium // pseudo-steady state.
2. Assumptions → Simplifications.
3. Determine whether the system $\underbrace{\text{temporal / spatial}}_{\text{lumped / distributed.}}$

Now, what are the general strategies to model a process? We will talk about the other type of system that is the lumped and the distributed parameter little bit later in this course or in the next lecture. But before that I want to enlighten upon that what are the possible strategies for modelling a process?.

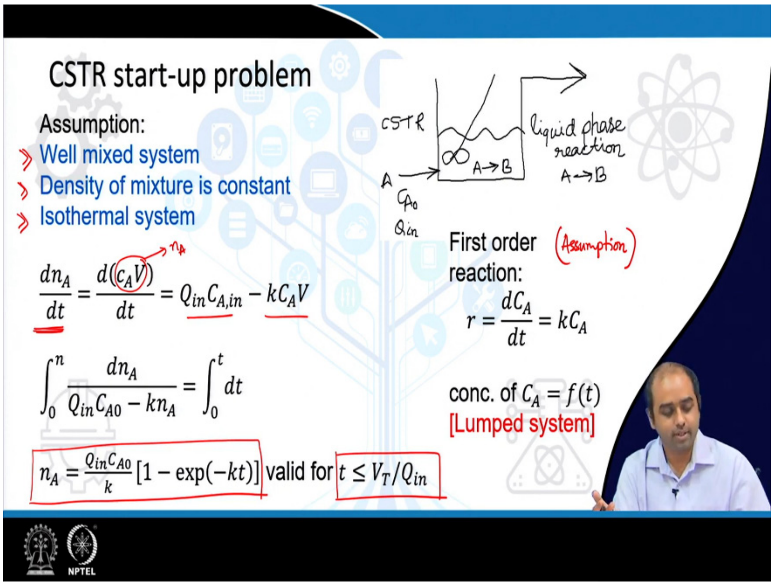
So, the first important thing that you should consider is whether the process is like transient or dynamic? it is at steady state or in equilibrium? or can be considered as a pseudo steady state? So, this is the first thing to determine for a process that what is the dynamics of the system.

Next important thing are the assumptions. Please understand that any mathematical model is subjected to the assumptions and they are only valid under the certain assumptions that you have considered for the model. So ideally, you should first try to have assumptions so as to simplify the problem and then slowly, you will try to relax the assumptions so that the problem is closer to reality.

So, we assume many things in a system to simplify the problem and that is how you should start with and slowly you should rework the problem, relaxing these assumptions. So, assumptions often help you with the simplifications but assumptions must and always be considered before starting to frame a model equation.

Next is that, determine whether the system is only temporal in nature or there is a spatial distribution of the variable. So, essentially this brings us to the class of whether it is a lumped parameter system or a distributed parameter system. Now, let us try to go through an example problem of a start-up of a CSTR. All of you have studied the CSTR in your chemical reaction engineering curriculum. So, here we will try to see that what happens during the start-up of a reactor, the start-up essentially is a condition or is a situation when you do not attain the steady state, when the system is not at a steady state and the system volume is also not attained.

(Refer Slide Time: 19:46)



CSTR start-up problem

Assumption:

- Well mixed system
- Density of mixture is constant
- Isothermal system

$$\underline{\frac{dn_A}{dt}} = \frac{d(\overset{n_A}{\boxed{C_A V}})}{dt} = \underline{Q_{in}C_{A,in}} - \underline{kC_AV}$$

$$\int_0^n \frac{dn_A}{Q_{in}C_{A0} - kn_A} = \int_0^t dt$$

$$\boxed{n_A = \frac{Q_{in}C_{A0}}{k}[1 - \exp(-kt)]} \text{ valid for } \boxed{t \le V_T/Q_{in}}$$

First order (Assumption) reaction:

$$r = \frac{dC_A}{dt} = kC_A$$

conc. of $C_A = f(t)$

[Lumped system]

So, in the case of the CSTR start-up problem, what we consider is that the system initially is not completely filled or the volume of the CSTR is not fixed and it is getting filled up that is what the start-up of the problem you mean by. This is a very common problem when you try to commission a CSTR. So, the volume may be so large that it takes a considerable amount of time for it to get filled up, but during that time it is possible that some reactions already start. So, how do you model this start-up phase of a CSTR?

Now, as I have already said, the system is dynamical in nature. There is a continuous change in the concentration because the volume is itself changing. It is not at a steady state. Start-up is not at a steady state. And next thing we have to determine is that what are the assumptions to the problem. Assumptions are very important. The first assumption we make is that it is a well-mixed system. So, if it's a well-mixed system, the concentration is uniform everywhere and it is homogeneous in nature. So, this also eliminates the criteria that the system is what we call is not a distributed parameter system. The other assumptions we make that the density of the mixture is constant and it is also an isothermal process. So, there is no energy related dynamics we are bringing in the picture.

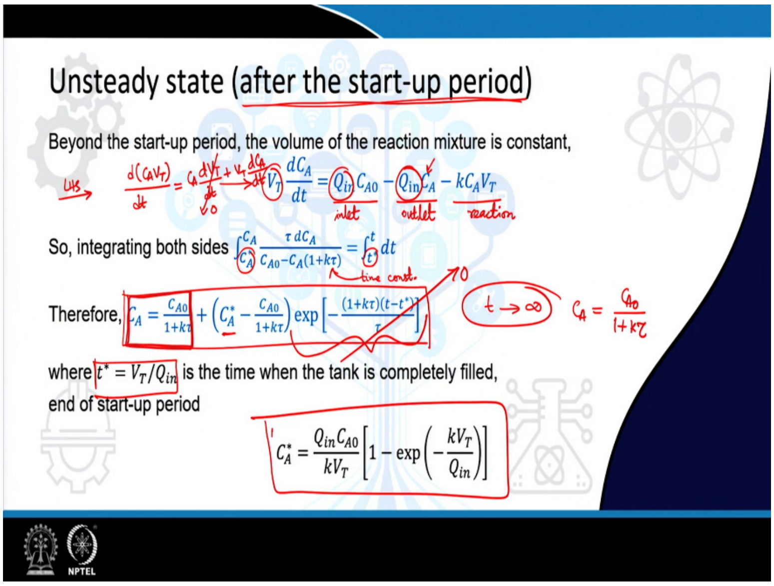
Now, since in this case the volume also changes with time, the concentration also changes with time. So, it is better to make a mole balance in this system. So, instead of writing in the normal CSTR balance, we try to write it in terms of the temporal derivative of the concentration but here we try to write the equation in terms of the mole balance. So, in this case we try to make a balance of the moles. The total change or the total accumulation of the moles is equal to the inlet minus the reaction.

Please note that there is no output of the system. So, something is only introduced to the system that is the rate of Q_in is the volumetric flowrate and I guess the symbols are self-explanatory and the decrease of the concentration or the moles is by the reaction. The reaction consumes the reactant A. We are trying to make a mole balance of the reactant A for the system. We have assumed this is also an assumption. I should say that we have also assumed that you are having a first order reaction in this system of order 1.

So, now if we try to make this in terms of the moles, we try to integrate this and we write this moles C_A V is nothing but the moles of the A. We can quickly rearrange this equation and we can come up with this expression of the this, you know, this how the mole in the system or the mole, the dynamics of the mole fraction or the molar concentration number of moles in the system changes.

Now, this equation is valid till the case the reactor is filled up, because once the reactor is filled up, the volume is constant. We will also talk about the phase which is known as the unsteady phase of the reactor, that once it is filled up, the volume of the reactor is constant. So, in that case we can deal with the concentration and we do not need to worry about this number of moles. So, this is the case when the time I mean, how do you find out the time that the start-up phase will exist? It is how much time it takes or the residence time of the system or how much time it takes at a particular flow rate to fill this reactor?

(Refer Slide Time: 23:50)



Unsteady state (after the start-up period)

Beyond the start-up period, the volume of the reaction mixture is constant,

$$\text{LHS} \rightarrow \frac{d(C_AV_T)}{dt} = C_A\underbrace{\frac{dV_T}{dt}}_{0} + V_T\frac{dC_A}{dt} \rightarrow V_T\frac{dC_A}{dt} = \underbrace{Q_{in}C_{A0}}_{\text{inlet}} - \underbrace{Q_{in}C_A}_{\text{outlet}} - \underbrace{kC_AV_T}_{\text{reaction}}$$

So, integrating both sides $\int_{C_A^*}^{C_A}\frac{\tau\, dC_A}{C_{A0}-C_A(1+k\tau)} = \int_{t^*}^{t}dt$ time const.

Therefore, $C_A = \frac{C_{A0}}{1+k\tau} + \left(C_A^* - \frac{C_{A0}}{1+k\tau}\right)\exp\left[-\frac{(1+k\tau)(t-t^*)}{\tau}\right] \rightarrow 0$ $\quad t \rightarrow \infty \quad C_A = \frac{C_{A0}}{1+k\tau}$

where $t^* = V_T/Q_{in}$ is the time when the tank is completely filled, end of start-up period

$$C_A^* = \frac{Q_{in}C_{A0}}{kV_T}\left[1-\exp\left(-\frac{kV_T}{Q_{in}}\right)\right]$$

So, moving ahead, trying to talk about the unsteady phase after the start-up of the reactor. After the start-up, there is also a finite time which is needed for the system to become steady. So, in this period there is an outlet, the volume of the reaction, the reactor is filled up. So, there is an outlet to these reactors as well as the inlet, and there is a reaction that is going in. So, this is the inlet to the reactor.

Then you have a part of the outlet. In both cases, the volume is the same because there is no mass accumulation in respect of the difference in the flow rate, whatever is in, what is equal to whatever is out and the outlet concentration is equal to the reactor concentration. And there is a reaction part to this.

Now, since the volume in this case is constant, we can easily take out the volume outside this derivative. So, the left-hand side is still d(C_A V_T). And if you do this, try to write in terms of the chain rule, you will get C_A into dV_T by dt plus V_T dC_A by dt. So, this part is 0 because the volume and the volume change does not exist in this case.

So, now you have this equation where you try to integrate on both sides. You can clearly understand that this tau is nothing but the time constant. I guess all of you are aware of this in terms of the CSTR configuration what do you mean by this tau. And you can find out that this expression of the concentration of the component A can be written in this form.

Now, what is this t*? In this case, t* is the period at the end of the start-up time, or it is a total start-up time in this case. So, when we try to integrate here, we start from a time that is not zeroth time. So, zeroth time is the start of the filling of the reactor. So, this unsteady period is at the end of the start-up period to a finite time, t. Similarly, the concentration at the end of the start-up period is written as C_A*. And that is what we write as C_A* here in this case. And you already know from the previous exercise that what do we mean by this C_A*.

So, this expression tells you that there is a time. So, if you try to plot this expression, and if you try to see it closely here, that unless t tends to infinity, that only when t tends to infinity, you will see that this exponential part in this problem, this part goes to zero when t is tending towards infinity. And then you get back to your classical equation of the CSTR that all of us are used to, in identifying a CSTR.

So, at t close to infinity, you will get CA is equal to CA naught 1 by k plus k tau. So, this helps you to understand that essentially how much is t close to infinity is a subject of interpretation because when this contribution to this exponential part is very low, you can consider that the system attains or evolves or is close to the steady state in this problem. But theoretically, it is exponential in nature. So, there will be some contribution, some unsteady contribution to this fact.

But anyway, so this is what do we mean by modelling the CSTR as it approaches towards a steady operation. So, first is the start-up phase. Then we have this unsteady phase. And then, as you can understand, on t tends to infinity you come to the case of the steady state scenario. So, with this, let us stop here for this lecture. In the next lecture, we will try to highlight a couple of more problems. And then we will talk about the distributed-lumped parameter systems and also about the differences of Stochastic and an example of a stochastic problem. Thank you. See you in the next lecture.