Chemical Reaction Engineering II

Prof. Ganesh Viswanathan
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 7
Catalyst Deactivation and Accounting for it in design – II

Friends, let us summarize what we learnt in the last lecture. We looked at catalyst deactivation, we defined what is catalyst deactivation? What is the activity of the catalyst, which characterizes the catalyst deactivation. We looked at different methods or different strategies or different ways, by which catalyst can get deactivated. For instance, we looked at sintering slash ageing process, which occurs because of long term exposure of the catalyst to the gas stream and the reactants.

Then we looked at coking or fouling which predominantly occurs, because of the deposition of carbonaceous material. When there is a catalytic reaction, that involves hydrocarbons. And we initiated discussion on the poisoning of catalyst, which a primarily occurs, because of the poisons; which may be present in the feed. Or in the reactant or the product itself may act as a poison. So, we started discussion on the strategies to characterize poison, when it is present in the feed. So, let us continue with that.

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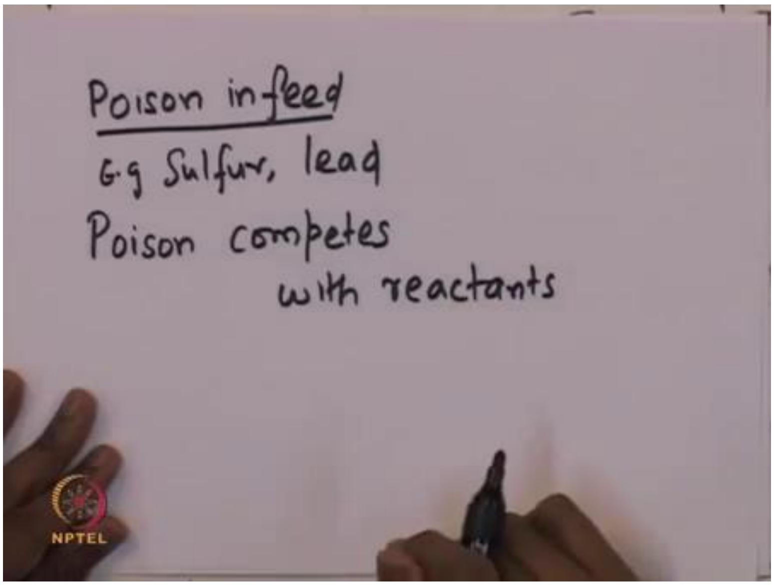

Poison in feed
e.g Sulfur, lead
Poison competes
with reactants

So the, a good example of that is the presence of sulfur or lead in the petrochemical feedstock's, which actually acts as a poison for the catalyst. So, example are sulfur and lead, which may be present in the petrochemical feedstock's. So, poison actually competes with the reactants for the catalyst site, with reactants for catalyst site. This is, because the poisoning process can actually occurs simultaneously, along with the catalytic reaction.

So, the active sites which are available for the reactants to go and adsorb, onto the catalyst site. And continue with the catalytic reaction, the poison also in a similar way is ready to go and bind itself, adsorb itself onto the catalyst site. So, therefore, it actually competes with the reactants for the available free active catalyst site. So, these possess a strong competition for the reactants. And that determines the extent of the deactivation of the catalyst.

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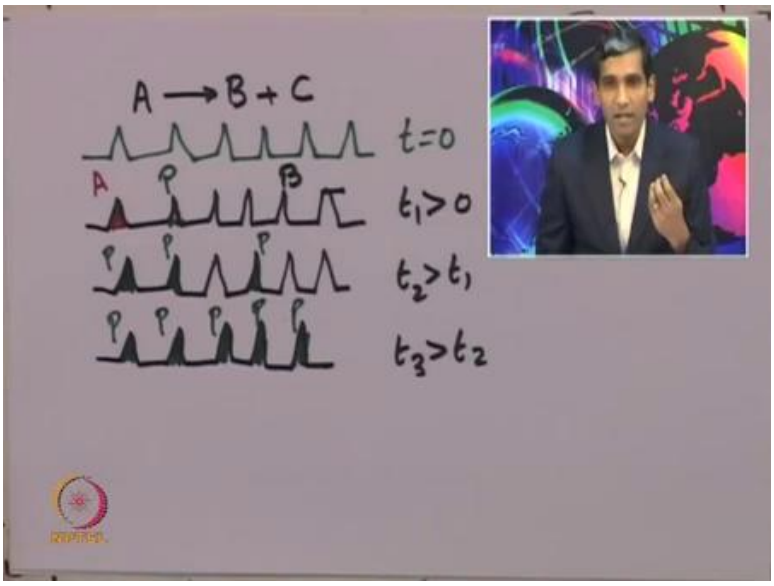

So, let us look at this cartoon, suppose if there is a reaction A going to B plus C of heterogeneous catalytic reaction. Now, if in the catalytic sites, suppose if these are the active catalyst sites, which are present at time t equal to 0 in the catalyst. And after the reactants start proceeding, and if these are the catalyst sites at time t 1, which is greater than 0. Then, the some of these sites may actually be, some of the sites will be containing this species A which is adsorbed onto to this surface.

So, species A and some other sites may be containing the poison, which is present in the feed stream. Suppose, if p stands for the poison, then this site may be contaminated with the poison. That is the active site is now blocked with the poison, which is adsorbed onto the active site. And may be some other site, may contain species B, which is basically the product, which is formed because of the catalytic reaction.

Now, if I look at a further larger time point t 2 which is greater than t 1. Then, you will have many more sites which are actually filled with the poison. So, we will have many other sites, which are filled with poison p. And therefore, the number of active sites, which are available for the reactants species to go and adsorb onto the active sites for the catalytic reaction, progressively decreases.

So, if look at further larger time point t 3, which is greater than t 2. Then, pretty much all the sites, all the active catalytic sites are now ((Refer Time: 04:47)) occupied by the poison, which is present in the feed. And therefore, the catalyst is completely deactivated at this time point t 3. So, it is very important to characterize a how this deactivation process occurs.

Because, the catalyst is normally used in the catalytic reactions are very expensive. And they cost a million dollars. And therefore, it is if one can avoid the poisoning of the catalyst and it saves a lot of money for the industry. And therefore, and also in it helps in maintaining the certain desired conversion, which is required for which is desired by the company.

So, therefore we let us look at what are the different mechanisms, that capture the poisoning process. And deduct deduce the rate law, which governs the poisoning process. And try to incorporate that into the reactor design. And this has a strong implications, in terms of how to avoid the poisoning process in the reactor.

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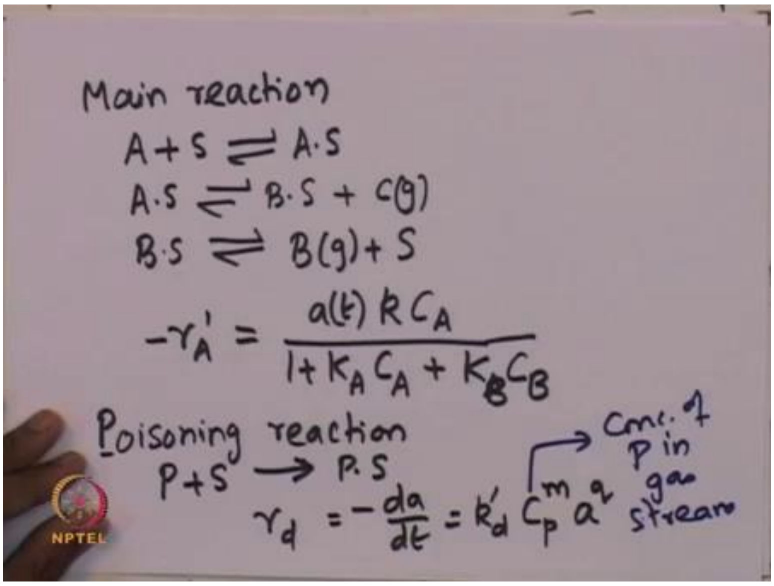

Main reaction

$$A + S \rightleftharpoons A \cdot S$$

$$A \cdot S \rightleftharpoons B \cdot S + C(g)$$

$$B \cdot S \rightleftharpoons B(g) + S$$

$$-r_A' = \frac{a(t)\, k\, C_A}{1 + K_A C_A + K_B C_B}$$

Poisoning reaction

$$P + S \longrightarrow P.S$$

$$r_d = -\frac{da}{dt} = k_d' C_p^m a^q$$

Conc. of P in gas stream

So, let us consider the reaction steps. So, there are three steps which is associated with this main reaction. So, the first step is the adsorption step, where species A, adsorbs onto the surface. And A S is basically the species A, which is adsorb to the catalyst site. And then the species A which is adsorbed onto the catalyst site, undergoes a catalytic reaction.

And leaves out product B, which is again adsorbed onto the catalyst surface plus a product c which goes into the gas stream. Then, this product B dot s, which is present in the on the catalyst site, gets disorb. And the product B goes into the gas phase, and leaving one catalyst site m vacant, one of the active sites.

Now, this particular reaction will typically have a rate law, which looks like this, which we have already seen in one of the earlier lectures. So, if A is the activity of the catalyst, then the rate of consumption of this species A. Because of this catalytic reaction, per gram mole of the catalyst per unit time is given by the activity of the catalyst A multiplied by the specific reaction constant and multiplied by the concentration C A divided by 1.

Plus the equilibrium constant for adsorption, desorption of the species A multiplied by the corresponding concentration plus the adsorption constant of species B multiplied by the corresponding concentration C B.

Note that, the main reaction is assumed irreversible here. Now, the poisoning reaction, the poison which is present, suppose p is the poison which is present in the gas stream, which is fed along with the reactants. Then, this poison is now going to participate in a poisoning reaction, which competes with the main reaction, for the active catalyst sites.

So, the poisoning reaction which occurs simultaneously along with the main catalytic reaction is as follows. So, p plus s which leads to binding of that particular poison, on adsorption of the poison onto the active site. And the rate law, rate of the decay, which is because of the poisoning of the catalyst active site is given by minus d a by d t. That is equal to the specific decay constant k d prime multiplied by C p m multiplied by a to the power of q, where C p is essentially the concentration of the poison, in the concentration of p in the gas stream. That is the concentration of the poison in the gas stream. So, the in order to estimate the, in order to integrate the find out the activity of the catalyst, we need to integrate the rate expression.

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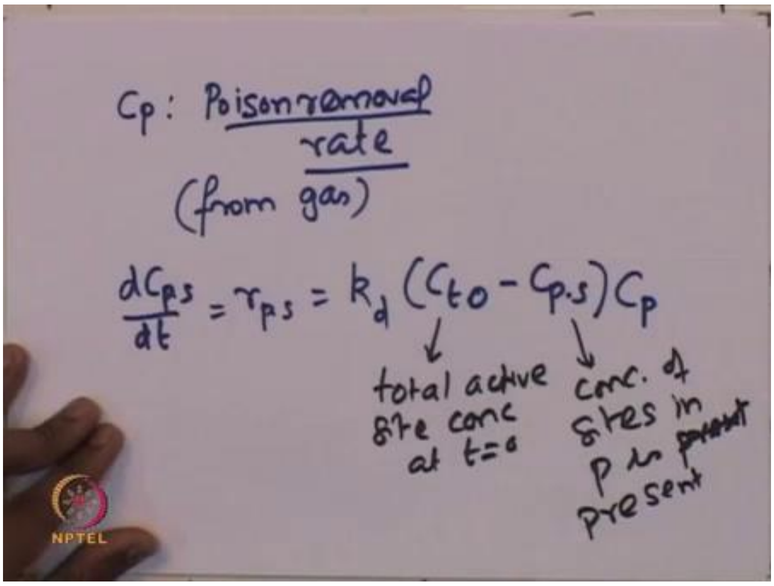

C_p: Poison removal rate (from gas)

$$\frac{dC_{ps}}{dt} = r_{ps} = k_d\,(C_{t0} - C_{p.s})\,C_p$$

total active site conc at $t=0$

conc. of sites in p is ~~present~~ present

But, before that we need to estimate what is the concentration of the poison, in the gas phase. So, for that we can simply write find out, what is the poison removal rate from the gas. And that provides a mechanism to characterize the dynamics of C p. So, d C p s by d t, which is basically the rate of change of the concentration of the poisoned active sites. And that is equal to r p dot s and that is equal to the specific reaction constant, multiplied by C t 0 minus C p dot s into C p.

So, this C t 0, C t 0 is the total active site concentration at t equal to 0. And C p s is the concentration of sites, in which p is present. That is p is adsorbed onto that is surface and C p is the corresponding gas phase concentration.

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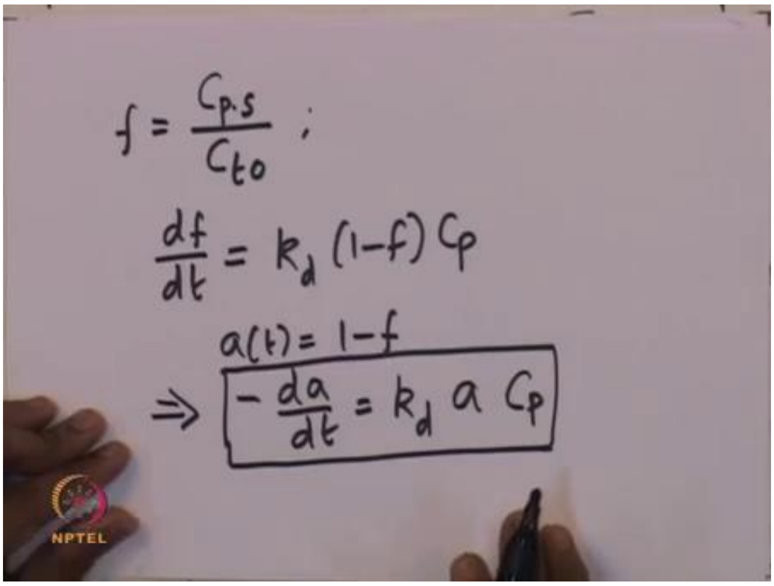

$$f = \frac{C_{p.s}}{C_{t0}} \;;$$

$$\frac{df}{dt} = k_d (1-f)\, C_p$$

$$a(t) = 1-f$$

$$\Rightarrow \boxed{-\frac{da}{dt} = k_d\, a\, C_p}$$

Now, if we define a new variable f, which is essentially the ratio the concentration of the sites onto, which the poison is adsorbed divided by the total concentration or the total concentration of all the sites, which is present at before the reaction is started. That is when the catalyst is fresh. Then, we can redefine this differential equation as d f by d t equal to k d into 1 minus f into C p.

Now, by definition the activity of the catalyst is essentially, the ratio of the reaction rate at a particular time. When, the catalyst is used up to a certain time divided by the reaction rate, as if it were a fresh catalyst. That is when the catalyst is unused. But, which is exactly equal to 1 minus f. So, therefore, the activity of the catalyst a t equal to 1 minus f and so we can rewrite this equation is minus d a by d t. That is equal to k d into a into C p.

So, this equation captures the activity of the catalyst, as a function of the gas phase concentration of the poison. And the reaction rate, on the decay rate constant. So, C p is a measurable quantity. So, if one can measure the concentration of the poison in the gas phase, we should be able to estimate the dynamics of the decay of the catalyst. So, let us look at how the catalyst activity changes in a packed bed reactor.

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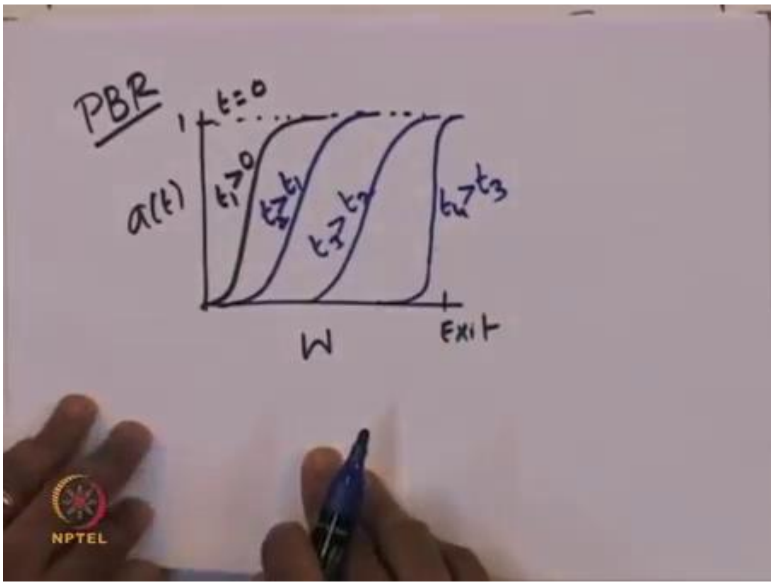

So, suppose there is a packed bed reactor. And suppose, if the this is the inlet of the packed bed reactor and this is the exit of the packed bed reactor. And if we want to look at the activity as a function of the weight of the catalyst at 0, when these gas stream does not enter the catalyst activity is almost one. And at time t equal to 0, when there is no reaction. The catalyst activity and all the locations is approximately equal to 1.

Because, the catalyst is not used and so all catalyst which is present inside is a fresh catalyst. So, it should be equal to 1. At some other time t 1, the profile would be like this. So, this is t 1 greater than 0. So, now some of these catalyst which is present, near to the inlet of the reactor, has now experienced reaction. And therefore, these catalyst will now start deactivating.

And so the initial part of the reactor of the catalyst will be deactivated significantly. And then this is the activity profile, that one would get. Now, if I further look at some other time t 2 which is greater than t 1. Then, this is the kind of profile you will get, where the reactor is been is expose to reactor is now used for conducting the catalytic reaction for a longer period of time.

And therefore, the more catalyst starting from the inlet of the reactor, would actually get deactivated. And so that is the kind of profile, that one would get. And then similarly you can profiles for a much larger time t 3, which is greater than t 2 would like this. And at a much later time t 4, which is greater than t 3, the profile would look like this.

So, therefore progressively the catalyst which is present inside the reactor will start getting deactivated. And that is what is captured in this profile here. So, next let us look at... So, far we looked at the poisoning, that is caused by the poison, which might be present in the feed. So, let us look at the poisoning, which is caused because of the reactants or the products itself.

So, remember we mentioned there are two different ways by which the poisoning can occur. One is because of the poisonous compounds which may be present, in the feed stream, and other one because of the nature of the reactants or products, which may itself become a poison for the active sites.

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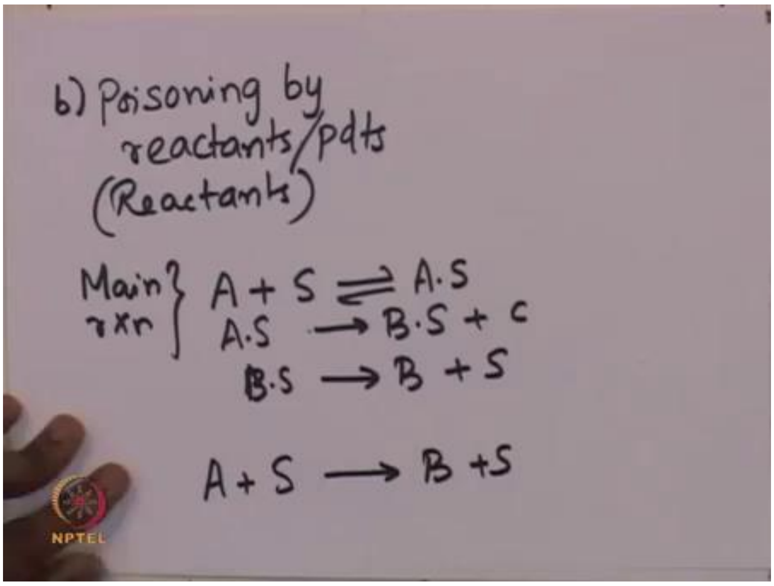

b) Poisoning by reactants/pdts (Reactants)

Main rxn
$$A + S \rightleftharpoons A \cdot S$$
$$A \cdot S \longrightarrow B \cdot S + c$$
$$B \cdot S \longrightarrow B + S$$

$$A + S \longrightarrow B + S$$

So, let us look at the second case of poisoning by reactants or products. So, the main... So, which means that the react, suppose let us consider the case of reactants, and the framework for if the products is the poison, the framework is exactly the same. So, let us specifically consider the case of reactant being a poison, and so the reactants are now, adsorbing onto the catalyst site for two purposes. One is for the catalytic reaction to occur and other one is basically to poison the catalyst site.

So, therefore the main reaction would be A plus S which is the catalytic site, which will basically lead to adsorption of the catalyst, onto the catalyst surface, catalytic site. And then A dot S would lead to B dot S plus let say some c. And similarly, B dot S can get desorbed to form B in the gas phase and release a catalytic site. So, this can actually be captured as A plus S essentially leading to B plus S. So, now the poison the reactant, because it also behaves like a poison, it now competes with the main reaction, in order to block the active catalyst site.

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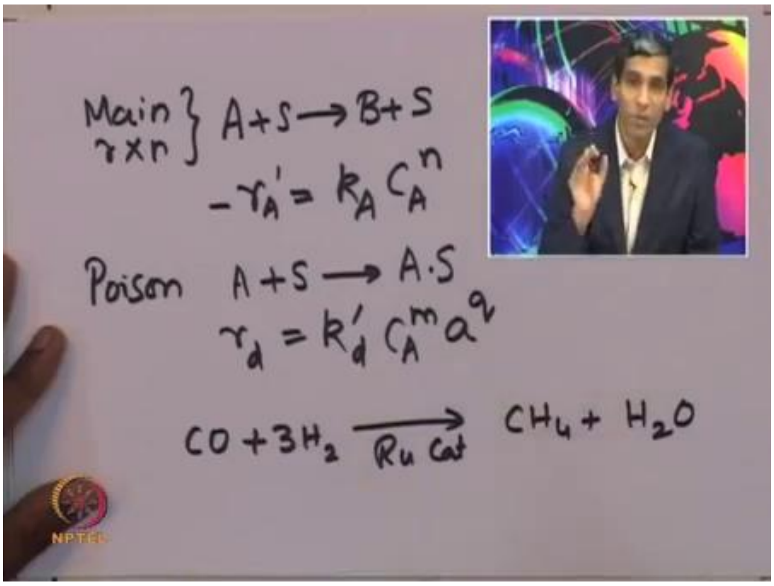

Main rxn $\Big\}$ $A+S \rightarrow B+S$

$$-r_A' = k_A C_A^n$$

Poison $A+S \rightarrow A\cdot S$

$$r_d = k_d' C_A^m a^q$$

$$CO + 3H_2 \xrightarrow[\text{Ru Cat}]{} CH_4 + H_2O$$

So, therefore the main reaction, which is A plus S leading to B plus S. Whose reaction rate can actually be represented as minus r A prime equal to k A into C A to the power of n. Let say for simplicity sake, then the poison reaction, there might be a poison reaction, which basically is A plus S which leads to A dot S, which poisons the catalyst site. And let us consider the rate of decay is equal to k d prime into C A to the power of m into a to the power of q. Let us assume that this is the decay law.

And a very good example of reactant itself, acting as a poison to the catalyst is the case of methane formation using carbon monoxide and hydrogen on a ruthenium catalyst, it leads to C H 4 and H 2 O. So, this is an excellent example of a situation, where the reactant which is the carbon monoxide, which goes and poisons the catalyst site. So, let us try to characterize this process, particularly for this example reaction.

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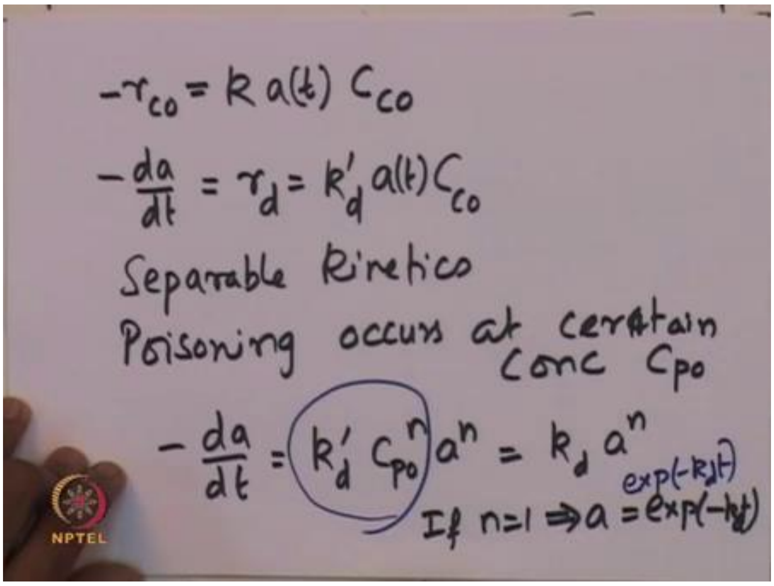

$-r_{CO} = k\,a(t)\,C_{CO}$

$-\frac{da}{dt} = r_d = k'_d\,a(t)\,C_{CO}$

Separable kinetics

Poisoning occurs at certain conc C_{po}

$-\frac{da}{dt} = \boxed{k'_d\,C_{po}^n}\,a^n = k_d\,a^n$

$\exp(-k_d t)$

If $n=1 \Rightarrow a = \exp(-k_d t)$

So, if the rate of reaction is given by minus r c o equal to specific rate reaction rate, multiplied by the activity a at as a function of time and multiplied by the concentration of the carbon monoxide. And the decay rate law is given by minus d a by d t. That is equal to r d, which is the rate at which the at catalyst gets deactivated. And that is the specific rate constant, multiplied by the activity, multiplied by the concentration of the carbon monoxide in the gas stream.

Now, if we assume that the kinetics is separable. So, if we assume separable kinetics and if we assume that the poisoning occurs at a certain constant concentration. So, if the poisoning at certain concentration C p o. Then, we can rewrite the rate law as decay rate law as d a by d t equal to k d prime into C p 0 to the power of n into a to the power of n. And that is equal to some k d.

So, we can now club these two constants together, we can club these two constants together in one constant multiplied in that is equal to k d into a to the power of n. So, if n is equal to 1. That means that the activity is given by exponential of minus k d into t. So, this is exponential of minus k d into t. So, that is the activity as a function of time of this particular case, when n is equal to 1.

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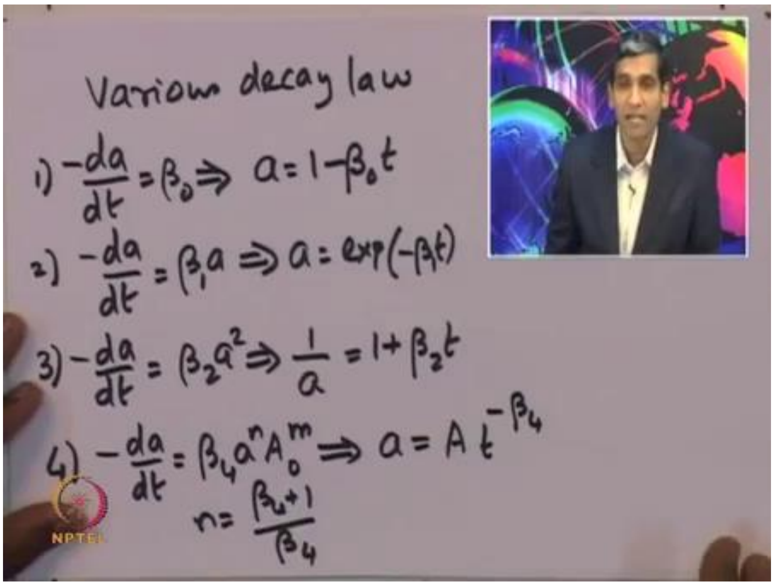

Various decay law

1) $-\frac{da}{dt} = \beta_0 \Rightarrow a = 1-\beta_0 t$

2) $-\frac{da}{dt} = \beta_1 a \Rightarrow a = \exp(-\beta_1 t)$

3) $-\frac{da}{dt} = \beta_2 a^2 \Rightarrow \frac{1}{a} = 1+\beta_2 t$

4) $-\frac{da}{dt} = \beta_4 a^n A_0^m \Rightarrow a = A t^{-\beta_4}$

$n = \frac{\beta_4+1}{\beta_4}$

So, there are various types of decay law, that have been proposed in the literature. And some of these are various decay law. So, common one is the one where the activity actually linearly changes with time. So, that is given by minus d a by d t equal to some beta naught. And when you integrate this expression, we find that a equal to 1 minus beta naught t. So, that is essentially a linear profile, linear dependence of the activity on time.

And this is actually a this kind of a decay has been observed for conversion of Para hydrogen on tungsten with oxygen as poison. So, this kind of a decay rate law has been observed for a reaction of conversion of Para hydrogen on tungsten with oxygen as the poison, that deactivates the catalyst that is tungsten here. Another rate law, that is been observed is the exponential rate law.

So, d a by d t that is equal to beta 1 a and integrating this expression, one would find that a equal to exponential of minus beta 1 into t. So, that is an exponential decay with respect to time. And this is been observed in the ethylene hydrogenation on a copper catalyst, with carbon monoxide as one of the poisons. So, this exponential decay has been observed in the ethylene hydrogenation, which is a very fairly well very common reaction a industry scale reaction.

And then the third type is minus d a by d t equal to it is the second order decay, the order of decay reaction with respect to the activity is two. And so the dependence of the activity on time is given by 1 by a equal to 1 plus beta 2 times t. And this is been observed in the cyclohexane dehydrogenation, on the platinum alumina catalyst, in addition to these decays laws, corresponding to independent deactivation.

The rate of deactivation can actually depend on the reactant or product concentration. For example, during hydrogenation of ethylene on palladium catalyst, ethylidene formation may reversibly block the active sites. And then the forth type forth class of deactivation kinetics is basically a power law behavior. So, where a power n into A naught to the power of m, where n is given by beta 4 plus 1 by beta 4.

So, that is the exponent and this on integration, one gets the an expression for A, which is basically some constant A into t to the power of minus beta by 4. So, it behaves like a power law of time. And this is been observed for cyclohexane aromatization, on nickel aluminum catalyst. So, now we have found the rate law for we have characterize the different types of deactivation of catalyst.

And we have found the rate law and for each of these cases. So, let us try to now implement the incorporate the rate law in a reactor design. So, let us consider a fluidized CSTR.

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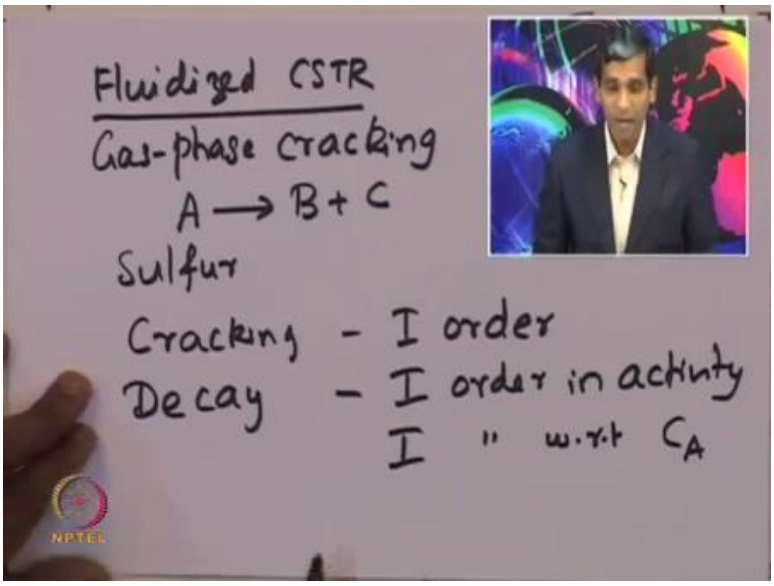

Fluidized CSTR

Gas-phase cracking

$A \longrightarrow B + C$

Sulfur

Cracking - I order

Decay - I order in activity

I " w.r.t C_A

And let us assume that a gas phase cracking reaction, where A goes to B plus C is occurring in this fluidized CSTR. And let us assume that the feed contains a sulfur, which acts as a poison for the catalyst. And also assume that, the cracking is a first order process. And if we assume that the decay catalytic deactivation or decay of the catalyst is first order with respect to, first order in activity. And it is first order with respect to concentration of species A in the gas stream.

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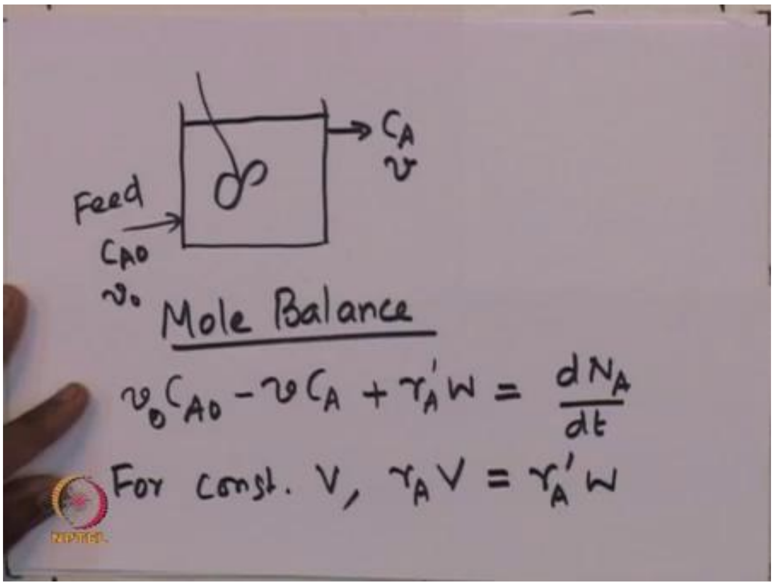

Mole Balance

$$v_0 C_{A0} - v C_A + r_A' W = \frac{dN_A}{dt}$$

For const. V, $r_A V = r_A' W$

So, now we can actually... So, the schematic fluidized CSTR it looks like this, where you have a fixed volume for the CSTR it is well mixed. And you have a feed which goes in. And let us assume that C A naught is the concentration of the feed at the inlet. And v naught is the volumetric flow rate of the feed at the inlet. And C A is the concentration of the product stream or concentration of species A in the product stream and v is the volumetric flow rate with which the fluid stream leaves the fluidized CSTR.

Now, a simple mole balance can be written for this system. So, the mole balance is the rate at which species enters the molar rate at which the species enters the reactor, which is v naught into C A naught. V naught has the units of volume per time. Let us say meter cube per time and the C A naught which is the concentration is in moles per unit volume minus whatever rate at which the molar rate, at which the stream leaves the reactor, which is v which is the volumetric flow rate, with which the stream leaves the reactor. And C A is the concentration at which it leaves the reactor. Plus the rate of generation of the species A, that is equal to the rate of change of the number of moles of A with respect to time, which is the accumulation term.

Now, for constant volume which is true for a CSTR for constant volume. The rate multiplied by rate in terms of the volume. That is, moles per unit volume per time, multiplied by the volume should be equal to the rate defined in terms of the catalyst weight. That is the moles of a reacted per gram weight of the catalyst per unit time, multiplied by the weight of the catalyst, so these two have to be equal. So, incorporating this equality into the mole balance.

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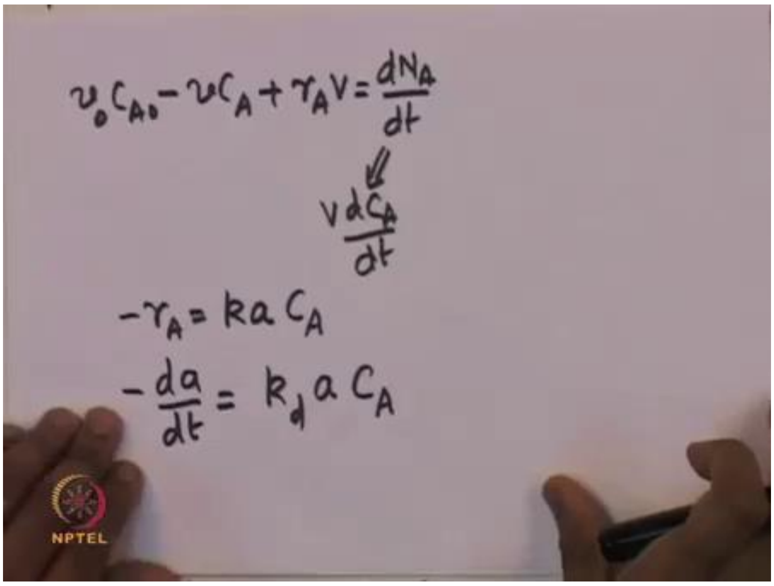

$$v_0 C_{A0} - v C_A + r_A V = \frac{dN_A}{dt}$$

$$\Downarrow$$

$$V\frac{dC_A}{dt}$$

$$-r_A = k a C_A$$

$$-\frac{da}{dt} = k_d a C_A$$

We can rewrite the mole balance as v naught into C A naught minus v into C A plus r A into v. And that is equal to d n a by d t. Now, d n a by d t can actually be written in terms of the concentration of the species, and so that will be v into d C A d t. So, now the rate at which the reaction occurs. That is the rate of consumption of species a is memos r A equal to the corresponding a specific reaction rate, multiplied by the activity of the catalyst multiplied by the concentration of the species C A.

And the corresponding decay law is given by d a by d t, that is equal to the decay constant multiplied by the activity of the catalyst, multiplied by the concentration of A in the gas phase. Now, if we know the rates of this reaction, that is the reaction rate. Then, next step we need to do in terms of designing the reactors, we need to use this stoichiometry and relate these terms here.

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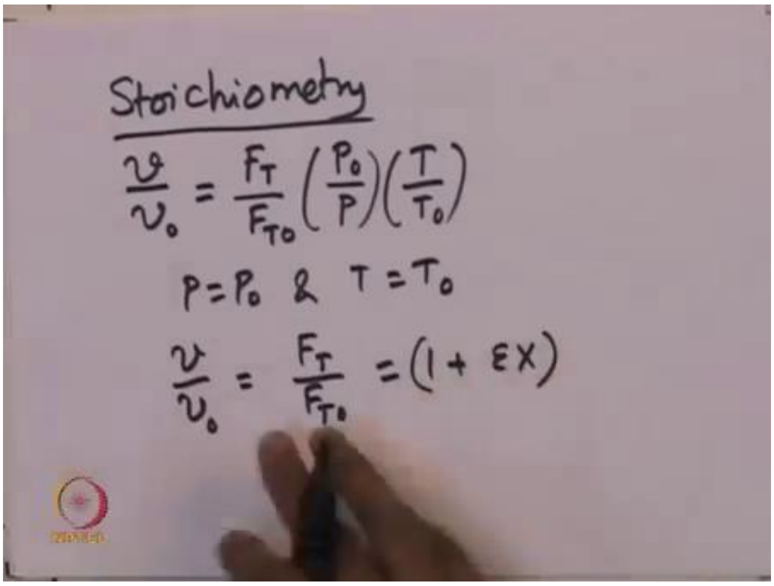

Stoichiometry

$$\frac{v}{v_0} = \frac{F_T}{F_{T0}}\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$$

$P = P_0$ & $T = T_0$

$$\frac{v}{v_0} = \frac{F_T}{F_{T0}} = (1 + \varepsilon X)$$

So, using stoichiometry we can find that the volumetric flow rate of the stream. That leaves the reactor divided by the volumetric flow rate of the stream. That enters the reactor should be equal to the molar flow rate F t with which these species leaves. Divided by the, it is the ratio of the total molar flow rate of the outlet stream divided by the total molar flow rate of the inlet stream. Multiplied by the p naught by p, which is the total pressure at the inlet divided by the total pressure at the outlet multiplied by T by T naught.

So, if at constant pressure if p equal to p naught and at isothermal conditions T equal to T naught. So, v by v naught simply reduces to F t by F naught F t naught which is nothing but 1 plus the net fractional change in the number of moles, because of the reaction multiplied by x.

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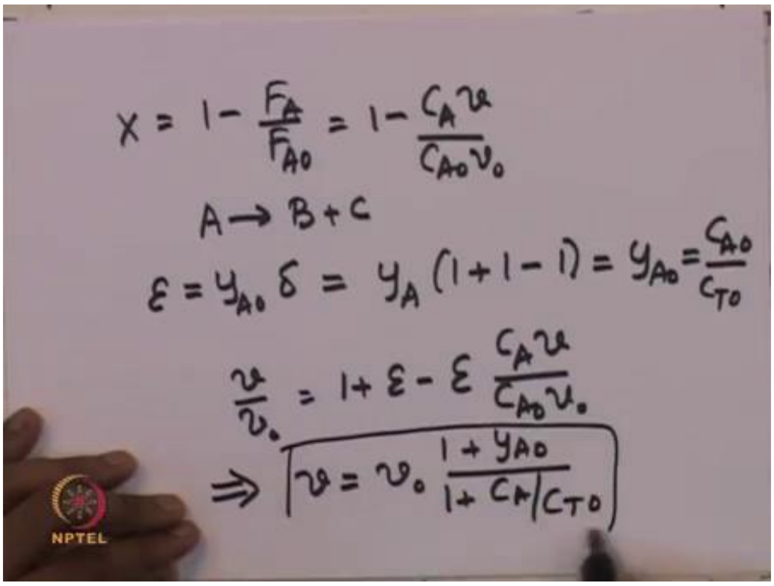

$$x = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{C_A v}{C_{A0} v_0}$$

$$A \rightarrow B + C$$

$$\varepsilon = y_{A0}\,\delta = y_A(1+1-1) = y_{A0} = \frac{C_{A0}}{C_{T0}}$$

$$\frac{v}{v_0} = 1 + \varepsilon - \varepsilon \frac{C_A v}{C_{A0} v_0}$$

$$\Rightarrow \boxed{v = v_0 \frac{1 + y_{A0}}{1 + C_A/C_{T0}}}$$

So, now the conversion x is equal to 1 minus F A by F A naught. So, that is the conversion and that is equal to 1 minus C A into v divided by C A naught into v naught. Now, remember that the reaction that we are looking at is A giving B plus C. So, therefore, the net fractional change in the number of moles is given by the overall mole fraction of A multiplied by these change in number of moles, which is equal to y A into 1 plus 1 minus 1.

That is equal to y A naught which is given by C A naught by C T naught, which is the C A naught is the concentration of the species in the inlet stream and C T naught is the total concentration at the inlet stream. So, by the using this expression we can rewrite v by v naught as 1 plus Epsilon minus Epsilon into C A into v divided by C A naught into v naught, which is...

And from here we can easily deduce that the volumetric flow rate of this stream that leaves the reactor should be equal to v naught into 1 plus y A naught divided by 1 plus C A by C T naught. So now plugging in all these volumetric flow rate expressions in terms of concentrations, etcetera into the mole balance.

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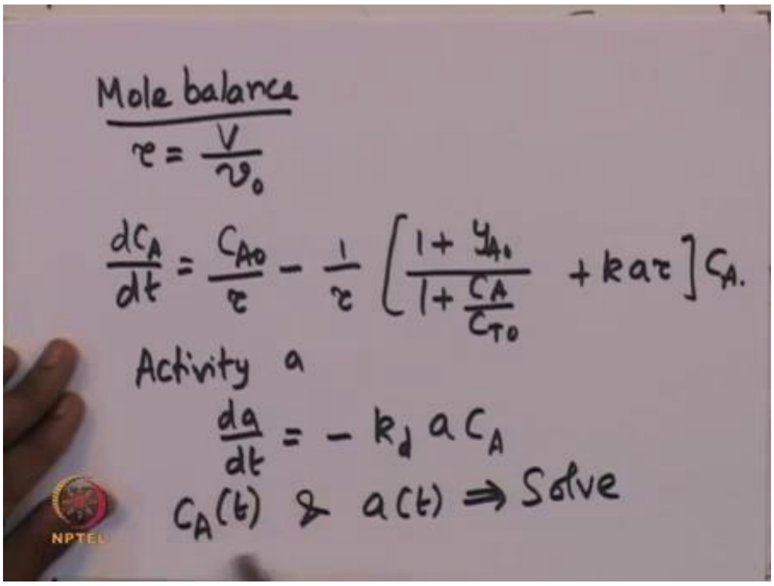

Mole balance

$$\tau = \frac{V}{v_0}$$

$$\frac{dC_A}{dt} = \frac{C_{A0}}{\tau} - \frac{1}{\tau}\left[\frac{1+y_{A0}}{1+\frac{C_A}{C_{T0}}} + ka\tau\right]C_A.$$

Activity a

$$\frac{da}{dt} = -k_d\, a\, C_A$$

$C_A(t)$ & $a(t) \Rightarrow$ Solve

We can rewrite the mole balance as after defining a residence time tau, which is the time that the fluid element times inside the reactor, which is given by volume of the reactor divided by the inlet volumetric flow rate. And so the mole balance will be d C A by d t, that is equal to C A naught by tau minus 1 by tau into 1 plus y A naught divided by 1 plus C A by C T naught plus k into a into tau into C A.

And the activity is given by activity a can be found from the decay rate expression for the catalyst. That is d a by d t equal to minus k d into a into C A. So, these two equations essentially characterize, the simultaneous, deactivation and the catalytic reaction, which is happening in the reactor. And so if one needs to obtain, the dependence of concentration on time. And the activity on time, then one needs to solve these two equations, solve the equation simultaneously.

And one should be able to obtain the concentration profile as a function of time. And the activity profile as a function of time. So, now we observed that the catalytic deactivation is a very serious problem, because it poses a strong major problem in terms of maintaining the conversion of the desired products. And as a result it has a strong effect on the economy of the company, which is actually producing that particular product.

So, therefore it has a strong effect on the economics of that particular product. And as a result choice of reactor is extremely important, which will help in minimizing or avoiding the deactivation process.

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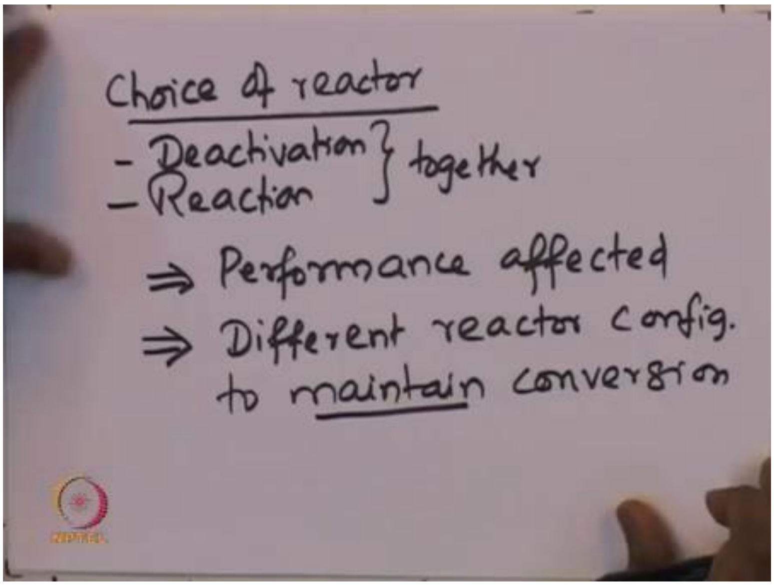

Choice of reactor

- Deactivation } together
- Reaction }

⇒ Performance affected

⇒ Different reactor config. to maintain conversion

So, the choice of the reactor. So, what we are going to discuss now is to look at how can we use a particular choice of a, how can we decide, what should be the choice of the reactor. That will help in minimizing the deactivation of the catalyst, and with the objective of maintaining the conversion of the desired product. So, we know that deactivation and reaction, they occur together they occur simultaneously.

So, therefore the performance is severely affected. And the as an offset one could actually use different reactor, configuration to maintain the conversion. So, what we are going to discuss now is to look at what are the different types of configurations, that one has to use, in order to minimize the deactivation of the catalyst. Or rather in order to maintain the conversion, desired conversion.

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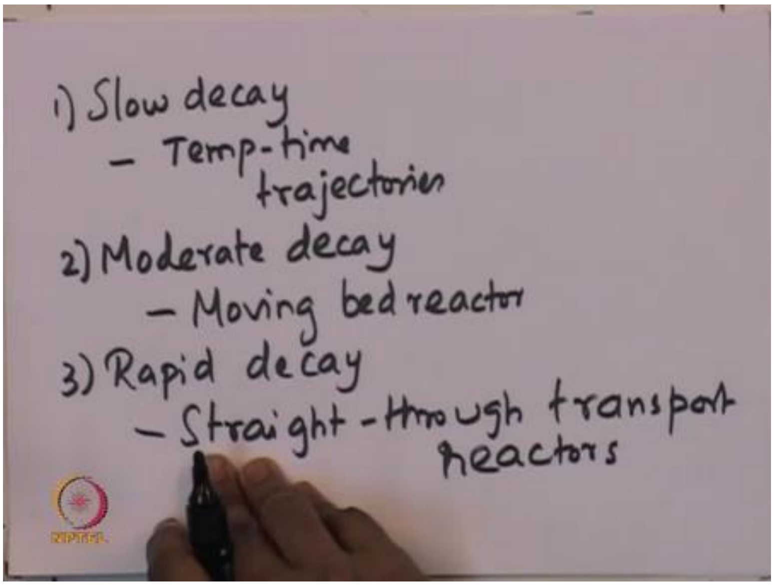

1) Slow decay
– Temp-time trajectories
2) Moderate decay
– Moving bed reactor
3) Rapid decay
– Straight-through transport reactors

So, suppose if the decay is very slow. So, naturally the choice of the reactor and the necessary steps that one has to take, depends upon the speed with which the catalyst gets deactivated. So, if the decay is very slow, then what really works is the is basically the using a temperature time trajectory, where the feed stream is constantly preheated at and the temperature is increased slowly, in order to minimize the deactivation. And thereby maintain the conversion of the reaction, which is happening inside the reactor.

Suppose if the decay is moderate, it is a moderate decay. Then, it is suggested to use a moving bed reactor. And we are going to look at the design of this, the moving bed reactor can be used in order to minimize the deactivation. And then if it is a rapid decay of the catalyst. Then, one needs to use a straight through transport reactors. This classification is based on the deactivation timescales, as dictated by the corresponding decay constant. So, let us look at the slow decay, the first case of slow decay, suppose if the catalyst is decaying very slowly.

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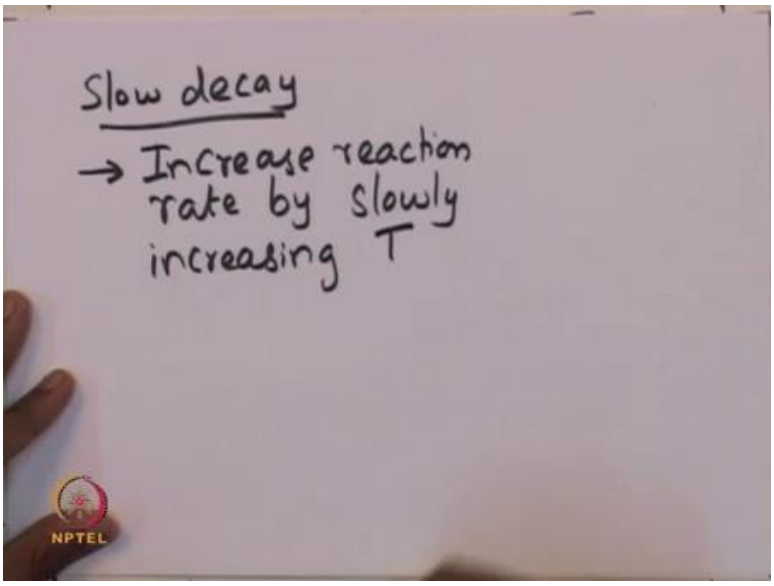

Slow decay

→ Increase reaction rate by slowly increasing T

So, if it is a slow decay system, then the in order to maintain a constant conversion. The strategy is to increase the reaction rate by slowly increasing the feed temperature. So, this by slowly increasing the feed temperature, one could actually increase a reaction rate. And thereby maintain the required conversion. And so the classical setup, which helps in such kind of a design is basically a fluidized bed. In fact, in many fixed bed reactors as well such a strategy is employed.

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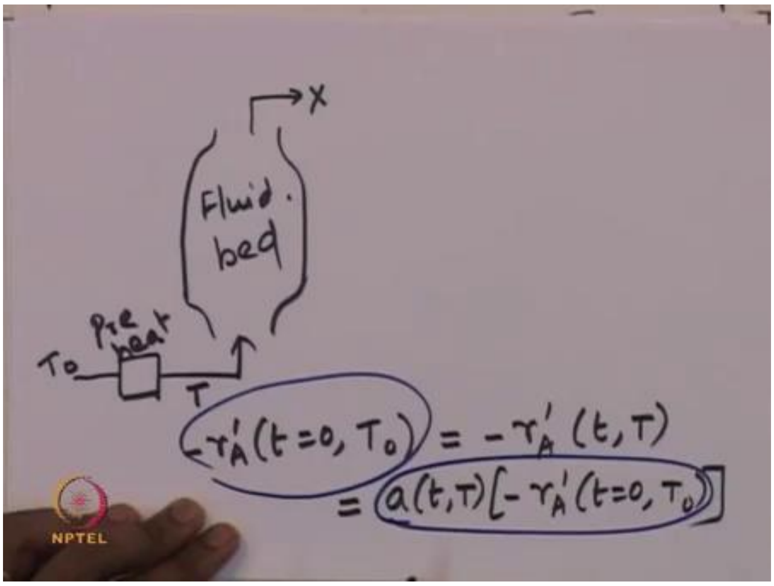

$$\boxed{-r'_A(t=0,T_0)} = -r'_A(t,T)$$
$$= \boxed{a(t,T)[-r'_A(t=0,T_0)]}$$

Suppose, if this is a fluidized bed, it is a fluidized bed reactor. And then a preheater is added to the inlet stream. So, suppose the inlet stream is entering the preheater at certain initial temperature t naught. Then, as the reaction proceeds the preheater constantly increases the temperature of the inlet stream. So, as to maintain a certain fixed conversion x.

So, which means that the reaction rate at t equal to 0. That is at the start of the reactor, at the temperature t naught should be equal to the reaction rate at certain other time and certain other temperature t. And in terms using the rate law, that we have derived for a catalyst deactivation, rate law for the reaction, when the catalyst deactivation is simultaneously occurring.

So, that will be a into t comma T. So, now the activity is a function of both time and temperature. And so minus r A into t equal to 0 comma T naught. So, these two quantities have to be equal, in order to obtain the desired conversion. This quantity must be equal to this quantity, in order to obtain the desired conversion in order to maintain the desired conversion.

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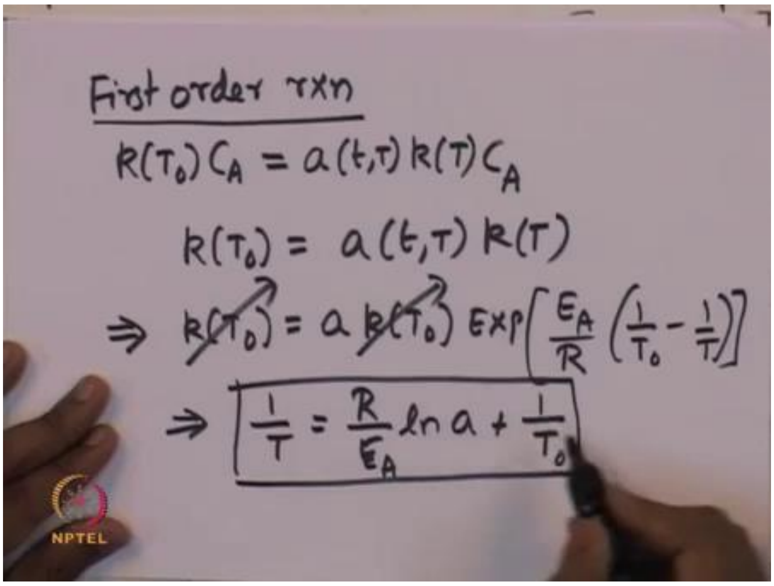

First order rxn

$$k(T_0)C_A = a(t,T)\,k(T)\,C_A$$

$$k(T_0) = a(t,T)\,k(T)$$

$$\Rightarrow \cancel{k(T_0)} = a\,\cancel{k(T_0)}\,\mathrm{Exp}\left[\frac{E_A}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]$$

$$\Rightarrow \boxed{\frac{1}{T} = \frac{R}{E_A}\ln a + \frac{1}{T_0}}$$

So, now if we assume that it is a first order reaction, and also if we neglect the concentration, variations. Then, we can write k of T naught into C A should be equal to the activity of the catalyst multiplied by the k. That is the specific reaction rate at a particular temperature, multiplied by the corresponding concentration C A. So, if we neglect the variations in the concentrations. Then, we can write that k t naught should be equal to a into k of T.

But, we know from the Arrhenius dependence of the specific reaction rate, that we can rewrite this expression as k into T naught. That is equal to a into k T naught multiplied by exponential of E A, which is the activation energy for that reaction divided by R into 1 by T naught minus 1 by T. So, cancelling these two, we can now find an expression that relates the local temperature. That is the temperature at which the reactor is being operated, with the activity and the temperature, when the reaction was started.

So, 1 by T should be equal to R by E A which is the activation energy of that particular reaction into lon a minus plus 1 by T naught. So, this is the relationship between the temperature at which the reactor has to be operated, and the activity as a function of activity and the initial temperature T naught.

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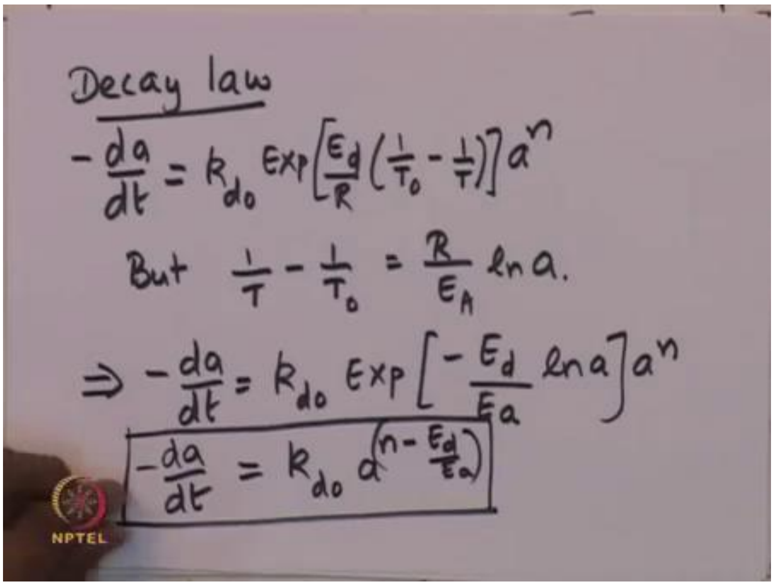

Decay law

$$-\frac{da}{dt} = k_{d_0} \exp\left[\frac{E_d}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right] a^n$$

But $\frac{1}{T}-\frac{1}{T_0} = \frac{R}{E_A}\ln a.$

$$\Rightarrow -\frac{da}{dt} = k_{d_0} \exp\left[-\frac{E_d}{E_a}\ln a\right] a^n$$

$$\boxed{-\frac{da}{dt} = k_{d_0} a^{\left(n-\frac{E_d}{E_a}\right)}}$$

So, now if we look at the decay law, which basically characterizes the deactivation of the catalyst. So, if we look at the decay law. So, minus d a by d t, minus d a by d t is given by k d naught multiplied by exponential of e d by R, which is again the a specific decay constant. This is also depends on temperature using the Arrhenius type expression into 1 by t naught minus 1 by T multiplied by a to the power of n.

But, we know using the rate law, we can relate the temperatures using the expression 1 by T minus 1 by T naught, that is equal to R by E A into lon a. So, by substituting this expression, we find that minus d a by d t. That is equal to, the specific deactivation constant multiplied by exponential of minus E d, which is the activation energy for the deactivation of the catalyst divided by E a into lon a into a to the power of n. So, this is equal to k d 0 into a raise to the power of n minus E d by E a. So, this expression provides a way to find out, what is the dynamics of the activity as a function of time.

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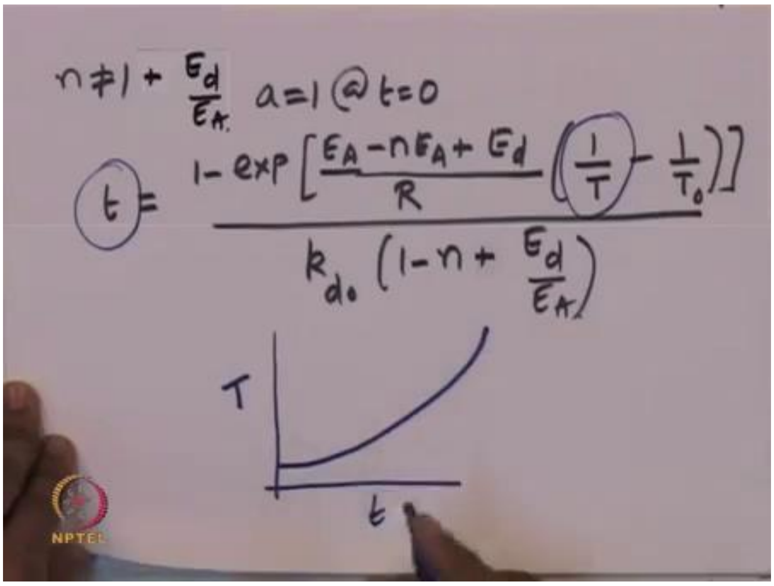

$n \neq 1 + \frac{E_d}{E_A} \quad a = 1 \ @ \ t = 0$

$$\boxed{t} = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R}\left(\boxed{\frac{1}{T}} - \frac{1}{T_0}\right)\right]}{k_{d0}\left(1 - n + \frac{E_d}{E_A}\right)}$$

Now, if n is not equal to 1, that is the order of the decay or deactivation, as a function of activity is not equal to 1, then with assuming that the activity is 1 at time t equal to 0. The expression can be integrated and found that t equal to 1 minus exponential of E A divided by E A minus n into E A plus E d. That is the activation energy for the decay divided by R into 1 by T minus 1 by T naught, the whole divided by k d 0 into 1 minus n plus E d by E a.

So, this expression provides a relationship as to, how the temperature has to be changed as a function time? So, this provides a relationship of, how the temperature has to be increased, in order to maintain a certain fixed conversion or desired conversion. Note that, this relationship is valid only for independent deactivation. So, this kind of an expression provides an industry operating person as to how much the temperature has to be increased. Or how much preheating has to be done.

In order to maintain the conversion of the desired products. So, now if I look at the, if I plot this as a function of time and temperature. So, this is the kind of profile, that I will get. So, if the catalyst deactivation is very slow. Then, I can maintain the conversion by actually increasing the temperature of the gas, that comes into the reactor. And the kind of profile and the kind of temperature, in raise as a function of time is captured in this graph here. So, suppose if it is a first order decay process, if the deactivation kinetics is directly proportional to the catalytic activity, and if the exponent is one.

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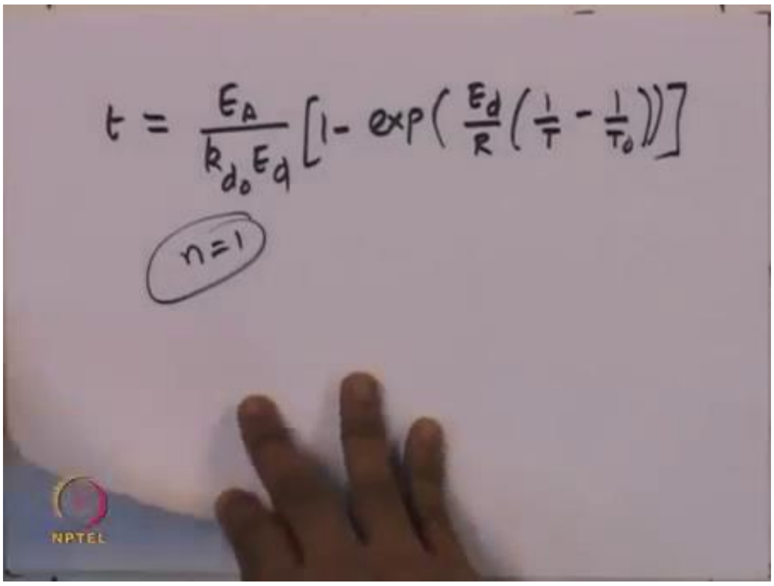

$$t = \frac{E_A}{k_{d_0} E_d}\left[1 - \exp\left(\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)\right]$$

$$\boxed{n=1}$$

Then, the relationship between the temperature and the time at which the temperature has to be changed is given by E A divided by k d naught into E d multiplied by 1 minus exponential of E d by R into 1 by T minus 1 by T naught. So, that is the expression one would get. And that sought of tells you, what is the how the temperature has to be increased as a function of time. When, n equal to 1 that is basically the first order dependence of the deactivation kinetics on the activity of the catalyst.

Now, as a next step, we look at what is the, what kind of configuration that one has to use, if the decay is moderate or a rapid deactivation of the catalyst.

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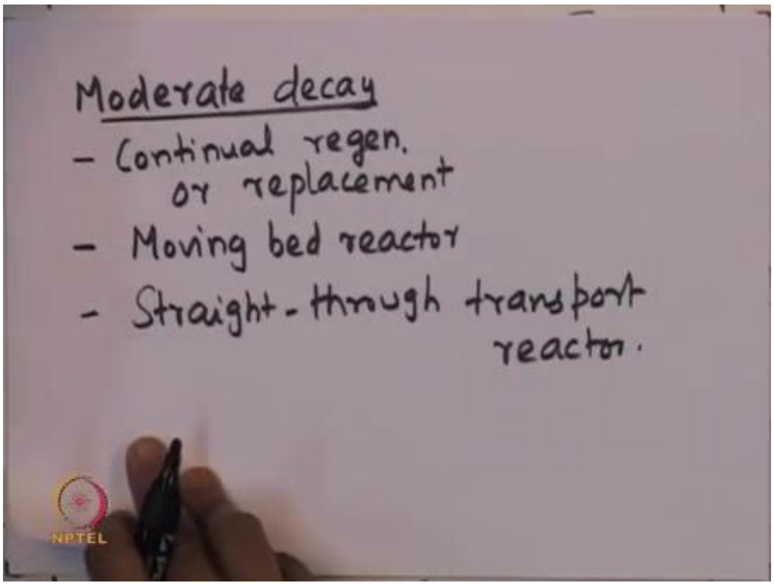

Moderate decay

- Continual regen. or replacement
- Moving bed reactor
- Straight-through transport reactor.

So, if we look at the moderate decay case. What is required here is, because the deactivation is fairly quick, fairly rapid. Then, there has to be a continuous regeneration or replacement of the catalyst, inside the reactor. In order to maintain a certain conversion, certain desired conversion of the products certain desired conversion. And therefore, the it is important to have a continual regeneration or replacement of the catalyst.

And there are two types of configurations, two reactor configurations have been use. So, one is the moving bed reactor. And the second one is the, straight through transport reactor, straight these are the two types of reactors which useful. When, there is a moderate or rapid decay of the catalyst, which is used in the catalytic reaction.

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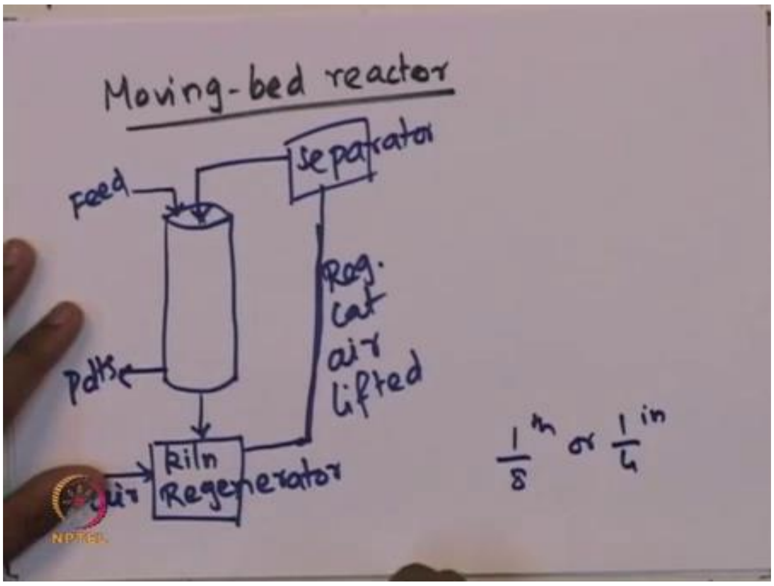

So, the moving bed reactor on the moving bed reactor is basically a reactor, where the catalyst is constantly replenished. And the way the catalyst is replenished is, suppose if this is the reactor, it is a cylindrical tube reactor. Suppose, this is the reactor, and the feed to the reactor is provided from the top. And the catalyst leaves the reactor and enters another chamber, which is called a kiln.

And this is used as a regenerator, which regenerates the spent catalyst, which is deactivated. And air is passed through this regenerator. And once the catalyst is regenerated; the regenerated catalyst is circulated back is the regenerated catalyst is air lifted into another chamber, which is called the separator chamber. So, it is a separator into the separator chamber.

And once the catalyst goes into the separator chamber, it pumps the catalyst back into the reactor. So, this is how the replenishment, constant replenishment of the catalyst occurs in a moving bed reactor. And this helps in maintaining the conversion. And the products are removed from the bottom of the reactor. So, the pellets that catalyst pellets that are typically used is about 1 8th inch or 1 4th inch. That is the typical size of the catalyst pellets, that is used in these kinds of reactors. So, now let us try to write model equations, in order to characterize the moving bed reactor. And thereby maintain the conversion of the reactants into products.

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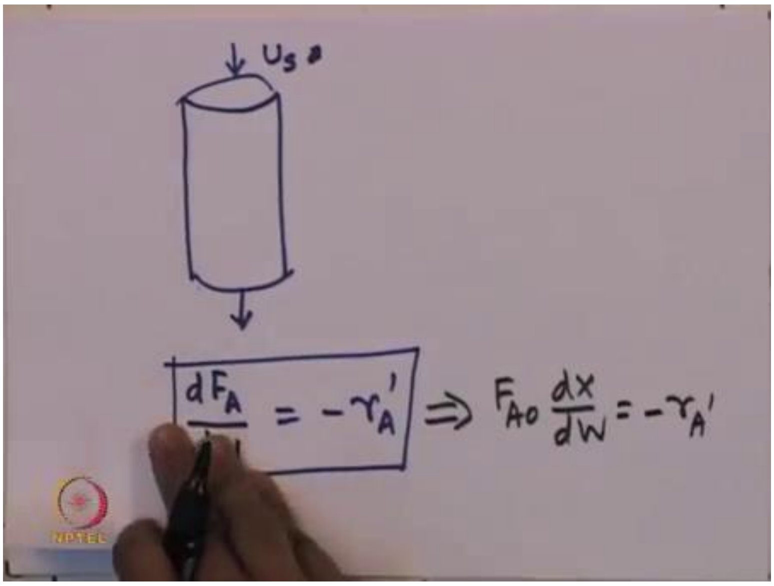

$$\boxed{\frac{dF_A}{dW} = -r_A'} \Rightarrow F_{A0}\frac{dx}{dW} = -r_A'$$

So, suppose if this is my reactor and if the catalyst enters the reactor, at rate of U s. That is the mass of catalyst per unit time. And if it leaves at the same range, then one can write a molar balance. And obtain an equation for the molar flow rate of the catalyst, molar flow rate of the species as a function of weight of the catalyst as... So, this equation molar balance, actually captures the dependence of the molar flow rate on the rate of the catalyst. And so this can be rewritten as F A naught into d x by d w equal to minus r A prime.

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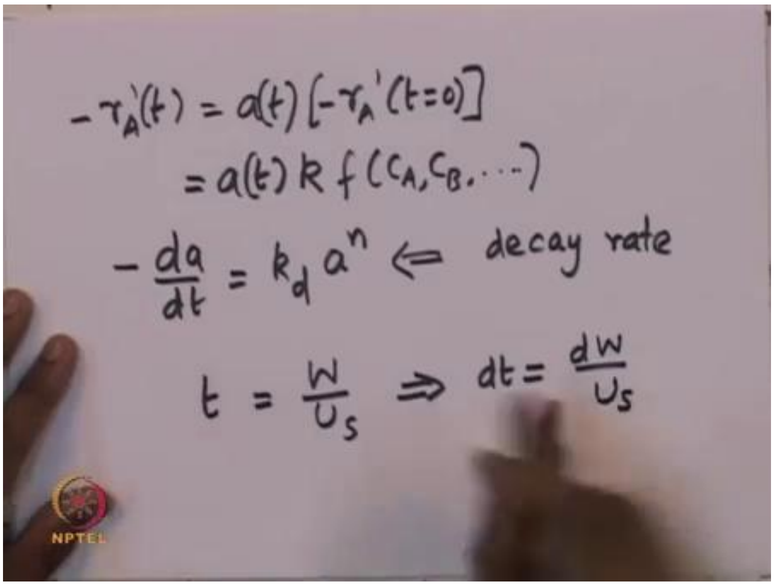

$$-r_A'(t) = a(t)\left[-r_A'(t=0)\right]$$

$$= a(t)\, k\, f(C_A, C_B, \ldots)$$

$$-\frac{da}{dt} = k_d a^n \Leftarrow \text{decay rate}$$

$$t = \frac{W}{U_s} \Rightarrow dt = \frac{dW}{U_s}$$

Now, the rate of the reaction is now can be written as minus r A prime is equal to some activity of the catalyst a. Multiplied by the rate of the reaction at time t equal to 0. So, therefore, it can be written as a of t, into the rate constant k. Multiplied by the some function of the concentration C A, C B, etcetera. And the deactivation kinetics is given by d a by d t is equal to the deactivation rate, rate constant multiplied by a to the power of n.

So, let us assume that this is the decay model. This is the decay rate, this decay rate law is a simplified form. And in general, the decay rate can depend on reactants slash product concentration. And so the contact time needs to be related with the weight of the catalyst, in order to characterize this particular reactor. So, the contact time of the catalyst t is given by W by U s.

And from here, we can estimate that the at a differential time the amount of catalyst that enters the reactor is given by d W by U s. So, from here we can now rewrite the mole balance, in terms of the catalyst, which enters the reactor. And also the decay rate law accordingly.

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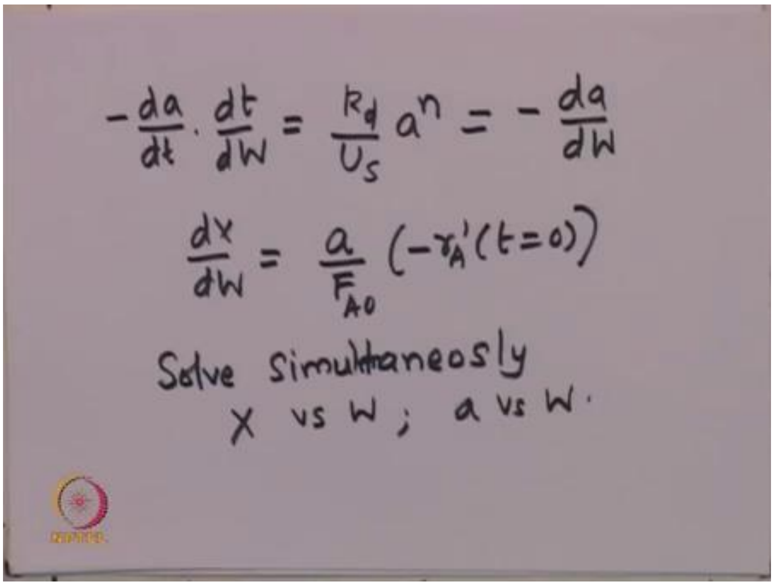

$$-\frac{da}{dt}\cdot\frac{dt}{dW} = \frac{k_d}{U_s}a^n = -\frac{da}{dW}$$

$$\frac{dX}{dW} = \frac{a}{F_{A0}}\left(-r_A'(t=0)\right)$$

Solve simultaneosly

X vs W ; a vs W.

And the decay rate law is now given by d a by d t into d t by d W equal to k d divided by U s into a to the power of n. And that is nothing but d a by d W. So, that relates the at decay of the catalyst as a function of the catalyst. That is entering the reactor and d x by d W is given by a by F A naught into minus r A prime at t equal to 0. So, these two equations need to be solved simultaneously to obtain X versus, the weight of the catalyst and a versus the weight of the catalyst.

So, that characterizes the moving bed reactor. So, once we know this, we can use this in design parameters, in order to appropriately design the catalyst. So, what we have seen in today’s lecture is, we have summarize the different types of deactivation of the catalyst. That is sintering ageing, fouling and or coking process and poisoning of the catalyst. And we looked into the details of the mechanism of two types of poisoning. One is poisoning, if the poison is present in the feed or if the reactant or the product itself acts as a poison.

And then we looked at a fluidized CSTR to incorporate the decay law, which is based on the poisoning of the reactor, and then poisoning of the catalyst. And then we proceeded to look at what are the different reactor configurations have to be used, because it depends upon the nature of the deactivation. If the deactivation is slow, then one can use the temperature time trajectory reaction system. And if it is moderate or a fast reactor, one has to fast decay. Then, one has to use a moving bed reactor or a straight through transport reactor.

Thank you.