Chemical Reaction Engineering - II

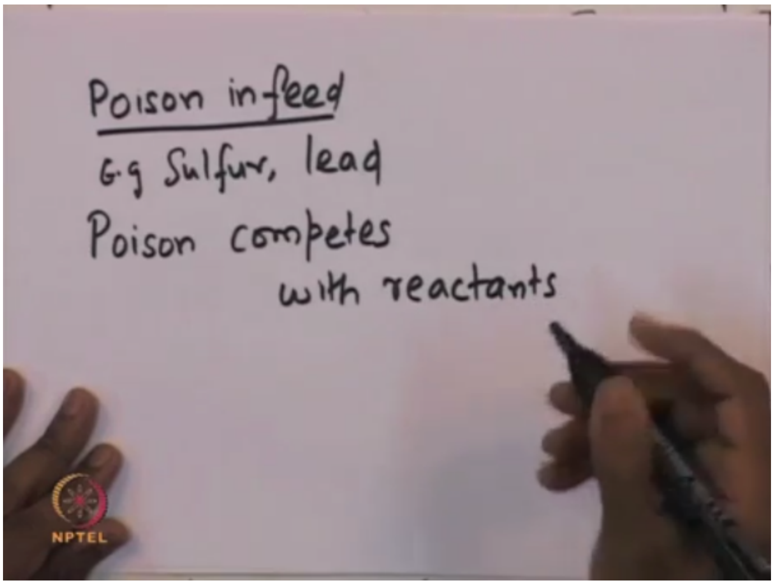
Prof. Ganesh A Viswanathan
Department of Chemical Engineering
Indian Institute of Technology - Bombay

Module - 3
Lecture - 15
Catalyst Deactivation III

Friends, let us summarise 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 characterises 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 / 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. Then we initiate a discussion on the poisoning of catalyst which primarily occurs because of the poisons which may be present in the feed or the reactant or the product itself may act as a poison. So, we start a discussion on the strategies to characterise poison when it is present in the feed. So, let us continue with that.

(Refer Slide Time: 01:53)

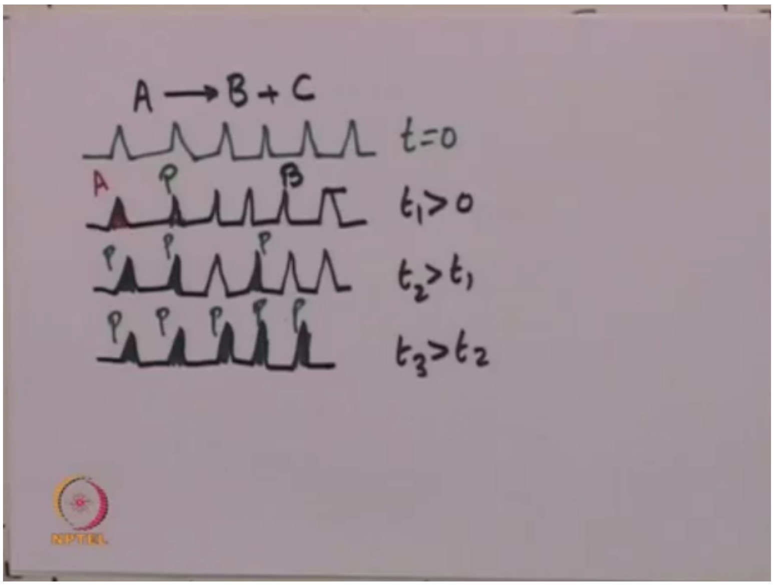


Poison in feed
E.g Sulfur, lead
Poison competes
with reactants

So the, a good example of that is the presence of sulphur or lead in the petrochemical feed stocks which actually acts as a poison for the catalyst. So, example are sulphur and lead which may be present in the petrochemical feed stocks. So, poison actually competes with the reactants for the catalyst site. This is because the poisoning process can actually occur 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 sites. So, therefore it actually competes with the reactants for the available free active catalyst site. So, this poses a strong competition for the reactants and that determines the extent of the deactivation of the catalyst. So, let us look at this cartoon.

(Refer Slide Time: 03:12)



Suppose, if there is a reaction A going to B + C. A heterogeneous catalytic reaction. Now if the catalytic sites, suppose if these are the active catalyst sites which are present at time t = 0 in the catalyst. And after the reaction starts proceeding and if these are the catalyst sites at time t 1 which is > 0, then the sum of these sites me actually be, some of these sites will be containing the species A which is adsorbed onto 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 these, 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 a species B which is basically the product which is formed because of the catalytic reaction.

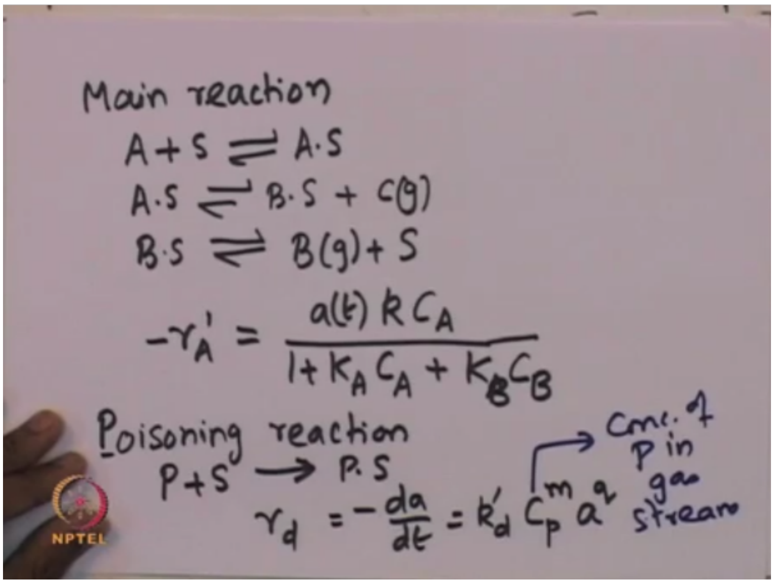
Now, if I look at a further larger time point t 2 which is > t 1, then you will have many more sites which are actually filled with the poison. So, we will have many other sites which are filled with poison p. And therefore, the number of active sites which are available for the reactant species to go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

So, if I look at further larger time point t 3 which is > t 2, then pretty much all the sites, all the active catalytic sites are now 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 characterise how this deactivation process occurs because the catalyst 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, then 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. So, let us consider the reaction steps.

(Refer Slide Time: 06:09)



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

$$P + S \rightarrow P \cdot S$$

$$r_d = -\frac{da}{dt} = k_d' \overset{\text{Conc. of P in gas stream}}{C_P^m}\, a^q$$

So, there are 3 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 adsorbed 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 + a product C which goes into the gas stream.

Then, this product B, B dot S which is present in the on the catalyst site gets desorbed and the product B goes into the gas phase and leaving 1 catalyst site end 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.

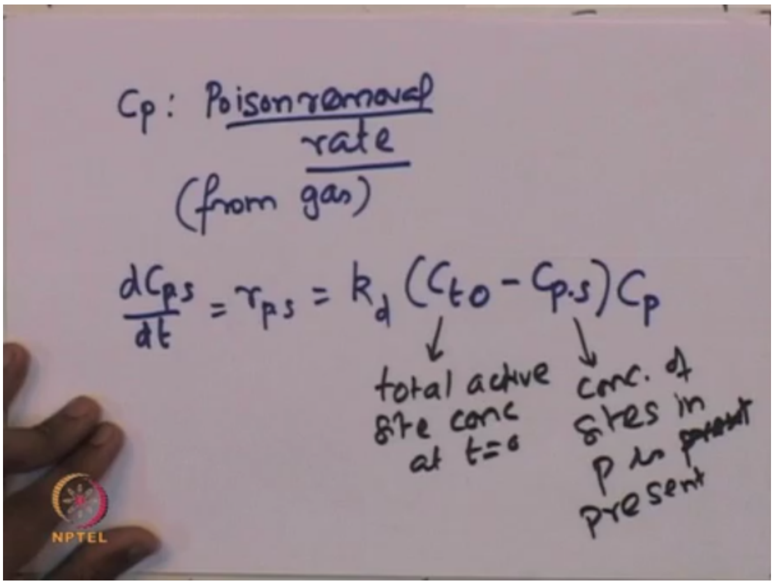
So, if we, if A is the activity of the catalyst, then the rate of consumption of the species A because of this catalytic reaction per gram mole of the catalyst per unit time is given by the activity of the catalyst a multiplied by the specific reaction constant and multiplied by the concentration C A divided by 1 + the equilibrium constant for adsorption desorption of species A multiplied by the corresponding concentration + the adsorption constant for 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 poison reaction which competes with the main reaction for the active catalyst sites. So, the poisoning reaction which occur simultaneously along with the main catalytic reaction is as follows.

So, P + 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 – d a by d t. That is = 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. But, before that we need to estimate what is the concentration of the poison in the gas phase.

(Refer Slide Time: 09:30)



C_p: Poison removal rate (from gas)

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

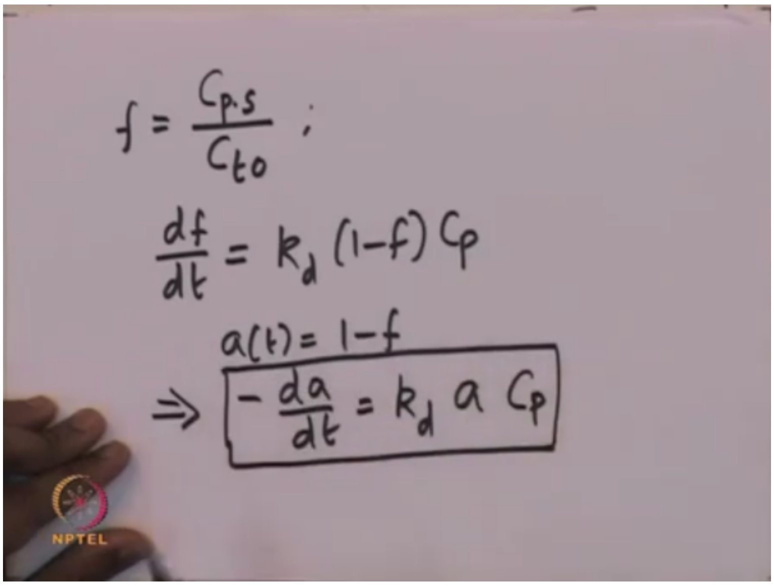
total active site conc at $t=0$

conc. of sites in p is present

So, for that we can simply write a, find out what is the poison removal rate. We can find out what is the poison removal rate from the gas. And that provides a mechanism to characterise 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 = r p dot s. And that is = the specific reaction constant multiplied by C t 0 – C p dot s into C p.

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

(Refer Slide Time: 11:06)



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

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

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

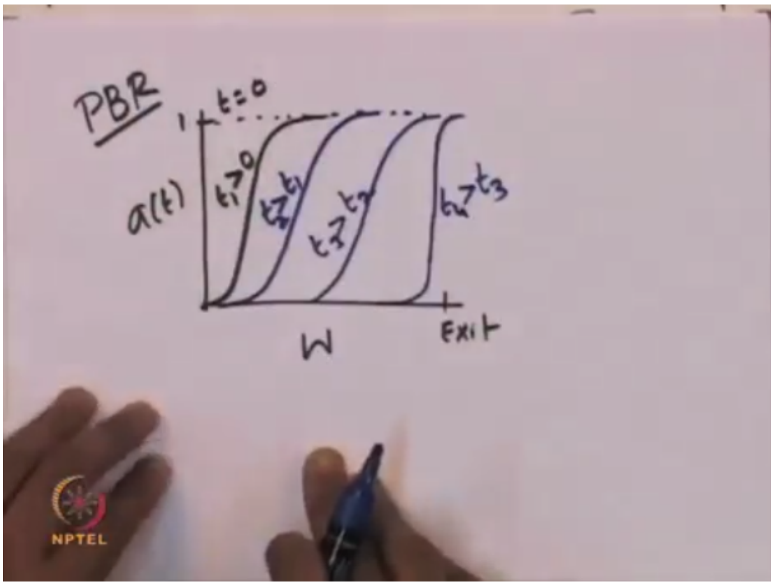
$$\Rightarrow \boxed{-\frac{da}{dt} = k_d\, a\, C_p}$$

Now, if we define a new variable f which is essentially the ratio of the concentration of the sites onto which the poison is adsorbed, divided by the total concentration or the total number, 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 = k d into 1 – 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 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 equal, which is exactly = 1 – f. So, therefore the activity of the catalyst a t = 1 – f. And so, we can rewrite this equation as – d a by d t, that is = 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.

(Refer Slide Time: 12:58)



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 you want to look at the activity as a function of the weight of the catalyst at 0 when the gas stream does not enter, the catalyst activity is almost 1. And at time t = 0 when there is no reaction, the catalyst activity and all the locations is approximately = 1 because the catalyst is not used and so all catalyst which is present inside is a fresh catalyst. So, it should be = 1.

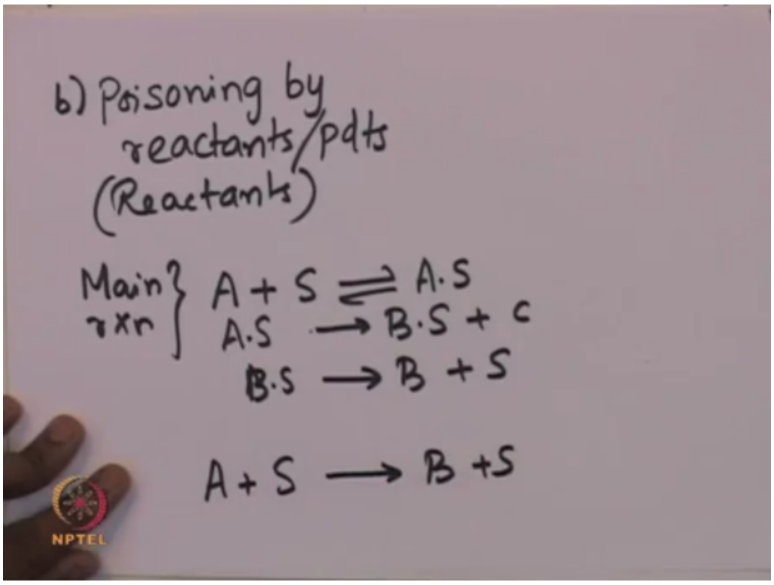
At some other time t 1 the profile would be like this. So, this is t 1 > 0. So now, some of these catalysts which is present near to the inlet of the reactor has now experienced reaction. And therefore the, these catalyst will now start deactivating. And so, the initial part of the reactor catalyst will 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 > t 1, then this is the kind of profile you will get, where the reactor is exposed 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 > t 2 would like this, would look like this. And at a much later time t 4 which is > 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, 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 2 different ways by which the poisoning can occur. One is because of the poisoned, poisonous compounds which may be present in the feed stream. Another one because of the nature of the reactants or products which may itself become a poison for the active sites.

(Refer Slide Time: 15:39)



b) Poisoning by reactants/pdts (Reactants)

Main rxn

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

$$A \cdot S \longrightarrow B \cdot S + C$$

$$B \cdot S \longrightarrow B + S$$

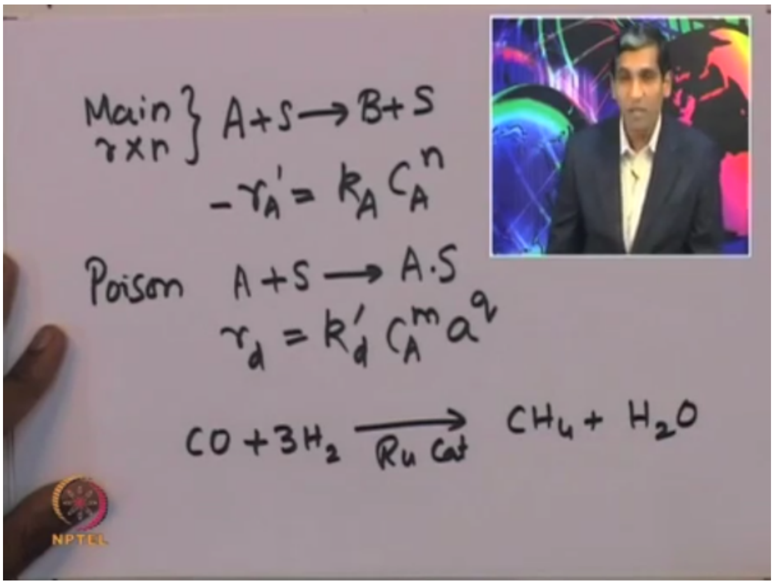
$$A + S \longrightarrow B + S$$

So, let us look at the second case of poisoning by reactants or products. So, the main, so which means that the, suppose let us consider the case of reactants. And the framework for, if the product 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 2 purposes.

One is for the catalytic reaction to occur, another one is basically to poison the catalyst site. So, therefore the main reaction would be A + S which is the catalyst site which will basically lead to adsorption of the catalyst onto the catalyst surface, catalyst, catalytic site. And then A dot S would lead to B dot S + let us 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 + S essentially leading to B + 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.

(Refer Slide Time: 17:19)



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

$-r_A' = k_A C_A^n$

Poison $A + S \rightarrow A.S$

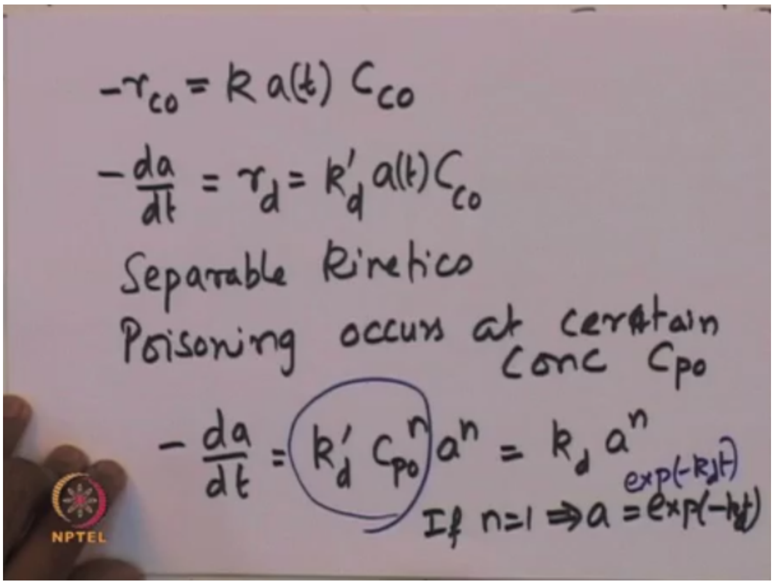
$r_d = k_d' C_A^m a^q$

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

So, therefore the main reaction which is A + S leading to B + S whose reaction rate can actually be represented as – r A prime = k A into C A to the power of n, let us say for simplicity sake. Then the poison reaction; there might be a poison reaction which basically is A + S which leads to A dot S which poisons the catalyst site. And let us consider the rate of decay is = 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 a methane formation using carbon monoxide and hydrogen on ruthenium catalyst, 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 characterise this process particularly for this example reaction.

(Refer Slide Time: 18:44)



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

$-\frac{da}{dt} = r_d = k_d'\,a(t)\,C_{co}$

Separable kinetics

Poisoning occurs at certain conc C_{po}

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

$\exp(-k_d t)$

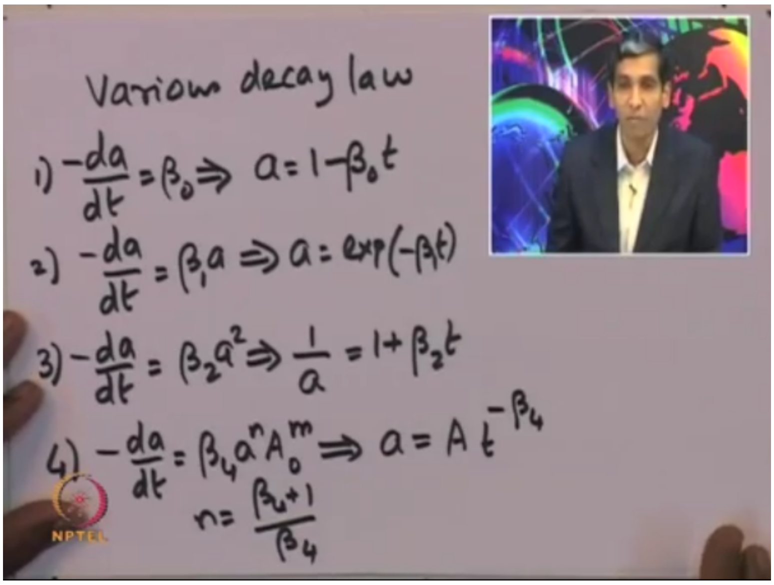
If $n=1 \Rightarrow a = \exp(-k_d t)$

So, if the rate of reaction is given by – r C O = 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 – d a by d t. That is = r d which is the rate at which the 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 you 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 = k d prime into C p 0 to the power of n into a to the power of n. And that is = some k d. So, we can now club these 2 constants together, we can club these 2 constants together in 1 constant multiplied in; that is = k d into a to the power of n.

So, if n is = 1, that means that the activity is given by exponential of – k d into t. So, this is exponential of – k d into t. So, that is the activity as a function of time, of this particular case when n is = 1. So, there are various types of decay law that have been proposed in the literature.

(Refer Slide Time: 20:54)



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

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

And some of these are, various decay law. So, a common one is the one where the activity actually linearly changes with time. So, that is given by – d a by d t = some beta nought. And when you integrate this expression we find that a = 1 – beta nought 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 or of tungsten on tungsten with oxygen as poison.

So, this kind of a rate law 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 has been observed is the exponential rate law. So, d a by d t, that is = beta 1 a. And integrating this expression one would find that a = exponential of – 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, a very common reaction, a industry scale reaction. And then the third type is – d a by d t =, it is the second order decay, the order of decay reaction with respect to the activity is 2.

And so, the dependence of the activity on time is given by 1 by a = 1 + beta 2 times t. And this is been observed in the cyclohexane dehydrogenation on the platinum alumina catalyst. In addition to these decay 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 fourth type, fourth class of deactivation kinetics is basically a power law behaviour. So, where a power n into a nought to the power of n, where n is given by beta 4 + 1 by beta 4. So, that is the exponent. And this while on integration one gets an expression for a which is basically some constant A into t to the power of – beta by 4. So, it behaves like a power law of time.

And this is been observed for cyclohexane urbanisation on nickel aluminium catalyst. So now, we have found the rate law for, we have characterised 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.