Heterogeneous Catalysis and Catalytic processes

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Lecture – 33

Good morning in my last lecture I was talking about catalyst deactivation. So, I will continue the same today also.

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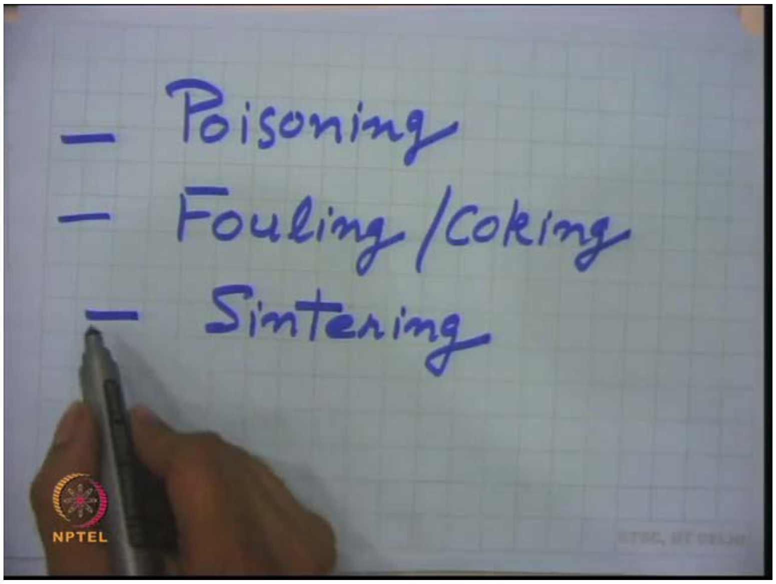

- Poisoning
- Fouling /Coking
- Sintering

I discuss the catalyst deactivation that the decrease in the activity of a catalyst with time on a stream and this may happen because of the Poisoning Fouling and Sintering. So, Poising is because the presence of the poison precursor that may be in the field itself it may be a product during the reaction. And, this is a kind of chemisorptions on the active side of the catalyst and there by decrease or destroy the active sides of the catalyst permanently. In, the case of Fouling it is the deposition of dult or mainly the cote material so, also known as coking, so carbonations material on the surface of the catalyst during the chemical reaction.

So, because of this the activity of the catalyst decrease however, this coking is a reverse bit process or the coke bud on the coke can be burned by using the carbon plus oxygen reaction. And, you can remove the carbon from the catalyst. So, regeneration is possible in this case the third case is the Sintering which is because of the high temperature and time. So, crystal size grow and the pore may destroy because of the long term duration when the catalyst is used in the reactor at high temperature. So, basically it is a re crystallization of the active centers of the catalyst. So, generally when you have you need to give some treatment in order to re generate the crystal structure of the catalyst. So, sometimes is it is possible but sometimes very difficult to regenerate the catalyst in this case.

So, depending upon the kind of the poison precursor or depending upon the type of deactivation in a catalyst the mechanism will be different. And, that is known as the deactivation mechanism and related to some function which is known as deactivation function. So, mechanism of coke formation when I say carbon formation it can be depending upon it can depend on the type of faddish stock it depends on the temperature or reaction conditions.

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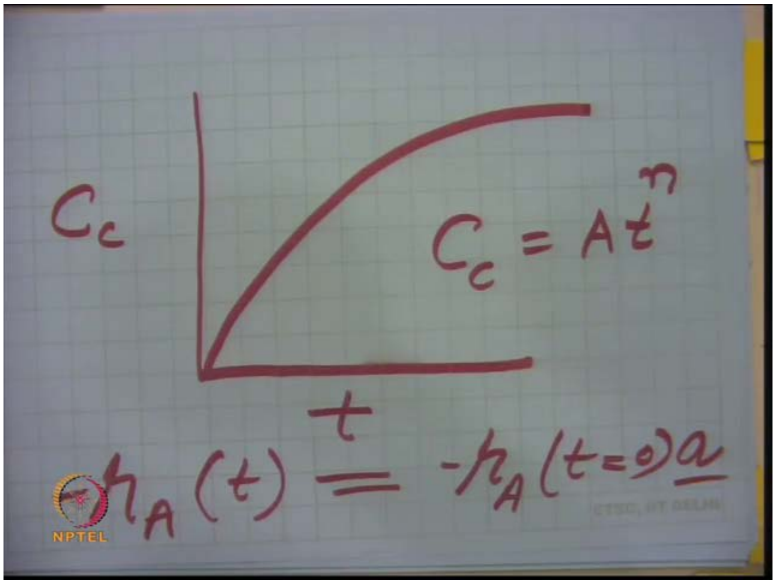

And, the mechanism may be different and accordingly the amount of coke formation on the catalyst may be different, which is discussed last time also that it is a kind of as entotic coke formation during a hydrocarbon conversion process. So, this is the amount of coke formed on catalyst as a function of time on stream. And, can be written some Cc is equal to A times t to the power n by some imperial co relation. So, n can be 0.5 and this can be 0.46 or 7.5 so different depending upon the type of faddish talk and temperature condition this may change. So, in general what I said that the coke formation mechanism exactly need to be established or discussed for given hydrocarbon for a given reaction over a given catalyst. So, in that case there are some common expression which are generally used to correlate the rate. Because, I told you that rate at any time t for the main reaction is rate at t is equal to 0. So multiplied by the activity or the deactivation function of the catalyst. So, this is the deactivation function and this is the rate when the catalyst is frost.

So, this is what here if you look at this is the rate when the catalyst is frost and this is a kind of activity A. Which, is defined general in terms of minus D by dt is equal to kd to the times A to the power n times some feed concentration or the co precursor concentration. So, the different mechanism may be available to define this value of y. And, this is a kind of Languor Hinsel hood Howzen Whatson expression which we have discussed earlier that this is a kind of temperature dependent term k 0 which is the read constant for the reaction. These, are the thermal dynamic equilibrium constants KA and KBCA is the concentration of the faddish talk and CB is the concentration of the product. And, this term is known as driving force for the reaction which we have already discussed.

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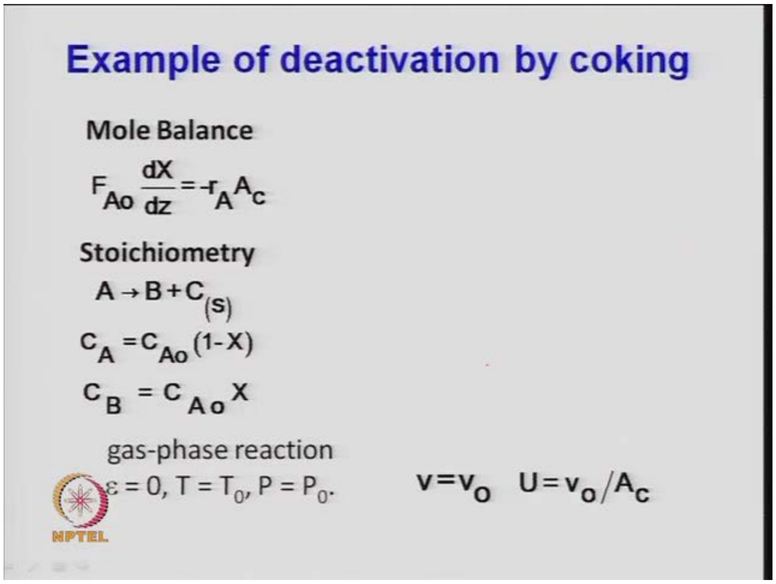

Example of deactivation by coking

Mole Balance

$F_{Ao}\frac{dX}{dz} = -r_A A_c$

Stoichiometry

$A \rightarrow B + C_{(s)}$

$C_A = C_{Ao}(1-X)$

$C_B = C_{Ao}X$

gas-phase reaction

$\varepsilon = 0, T = T_0, P = P_0.$ $v = v_O$ $U = v_O/A_c$

So, when you need the kinetics for the deactivation reaction or when you want to find out activity with time on stream. So, one needs to write a mole valence equation I usual in the reactor design. So, this is a kind of mole valence equation here FA naught dX A by dz is equal to minus rA times AC. Or, one can write it FA naught dXA by dv because Ac into dz is dv volume of the reactor in differential form and, that is minus rA rate of reaction per unit volume of reactor.

So, one can write this expression in the form of per unit mass of the catalyst also so that it becomes FA naught dxA by dw is equal to minus rA dash. Where, rA dash is rate of reaction per unit mass of the catalyst. So, this true for a stoichiometry which is given here, A converts to B which is a product and C is a solid material a carbon or coke concentration expressions all of you know now cA is equal to cA naught 1 minus XA. Because, it is a constant volume system here one mole of this gives one mole of the product, which is generally the gases phase and CB is the moles of p formed. So, that is reported in terms of the conversion so CA naught times X concentration of B. All, of you know that moles FA at any times if you write FA naught initially is CA naught initial concentration times the volumetric feed rate which we have already discussed in the design.

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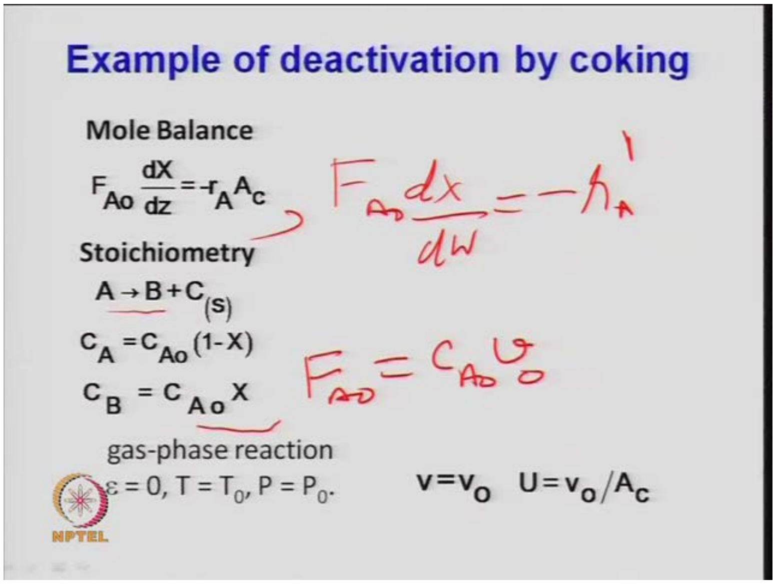

Example of deactivation by coking

Mole Balance

$F_{Ao}\frac{dX}{dz} = -r_A A_c$

$F_{Ao}\frac{dx}{dW} = -r_A'$

Stoichiometry

$A \rightarrow B + C_{(S)}$

$C_A = C_{Ao}(1-X)$

$C_B = C_{Ao}X$

$F_{Ao} = C_{Ao}\upsilon_o$

gas-phase reaction

$\varepsilon = 0, T = T_0, P = P_0.$ $v = v_o$ $U = v_o/A_c$

So, if you look at this rate equation this is your design equation or one can write as I said in the form of FA naught dx by dw is equal to minus rA dash for the catalytic reaction generally we use this. But, wd is the mass of the catalyst which will depend on the density of the catalyst in the bed row B times this volume dv. So, dv is a C times dz. So, one can write the expression in either form v is constant volume system volumetric feed rate.

And, superficial gas velocity is also important when we look at a design of a system when the catalyst deactivates. So that is volumetric fluoride divide by the area of cross section of the reactor the F silent is the fresnel change in volume and since it is a constant volume system. So, there is no change in the volume during the reaction t is temperature under isothermal condition so t0 and p is the pressure is 0.

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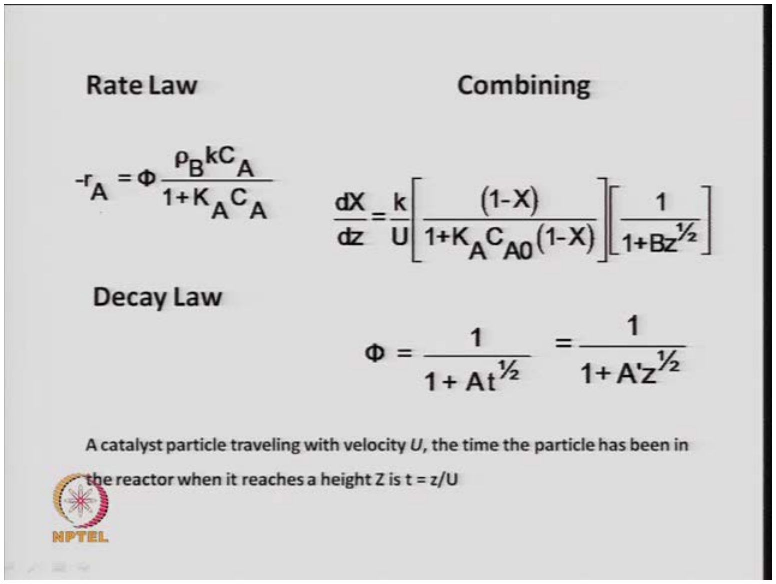

Rate Law

$$-r_A = \Phi \frac{\rho_B k C_A}{1+K_A C_A}$$

Combining

$$\frac{dX}{dz} = \frac{k}{U}\left[\frac{(1-X)}{1+K_A C_{A0}(1-X)}\right]\left[\frac{1}{1+Bz^{1/2}}\right]$$

Decay Law

$$\Phi = \frac{1}{1+At^{1/2}} = \frac{1}{1+A'z^{1/2}}$$

A catalyst particle traveling with velocity *U*, the time the particle has been in the reactor when it reaches a height Z is t = z/U

So, this is what the expression in terms of rate law so one can write minus rA which is a deactivation function times there are density of the catalyst in the bed times. But about, the kC A divide by 1 plus kC A which is at any time. And, assuming that the second term kC A with C a minus CB. So, here we have assumed that the reaction is irreversible. So, one can very easily write this expression. And, as I discussed that this is your dx A by tz which is written in this expression here so we have substituted this in form of d x a by d z so your expression which comes out in this form dx A by dz. Because, FA naught dx A by dz is equal to minus rA into AC. So, one write this rA in terms dx A by dz and I told that this deactivation function most of the time these are empirical so, relation. So, here the deactivation function is defined by 5 is equal to 1divide by 1plus At to the power ½. So, where this is an kind of empirical expression where this A is a constant and n which I defined earlier is 1 by 2 here.

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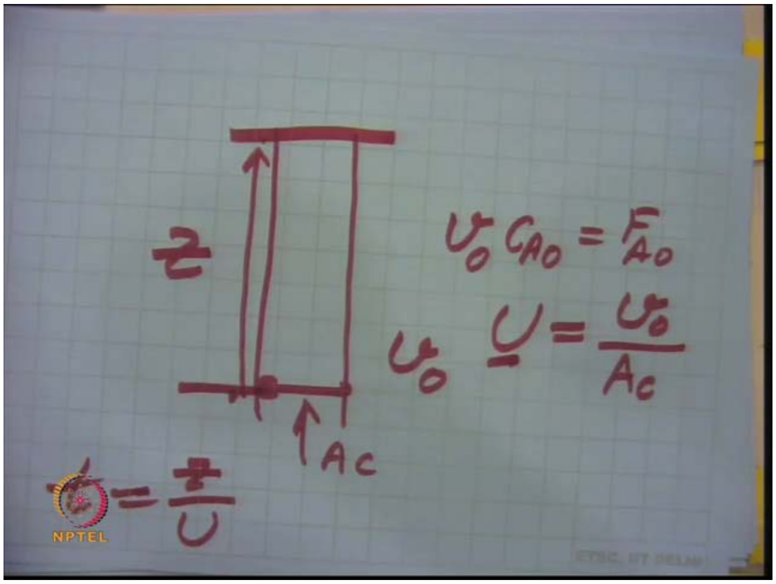

And, time which we are talking again here in a reactor. This, depends on the superficial velocity so v naught suppose is the volumetric feed rate and AC is the area of cross section of this tube. So, I define that v naught volumetric florid is related to some molar florid so that v naught into CA naught concentration is your total molar florid of A that is one term. Second term is this, superficial gas velocity so superficial gas velocity U is defined by volumetric feed rate divide by the area of the cross section. And, this U superficial gas velocity if I say the z is the height of the reactor height of the reactor. That, this time to travel from this point to this point is this time when the catalyst gets deactivated. So, what is the activity of the catalyst after this time t that can be correlated in terms of height of the reactor and the superficial gas velocity. So, one can correlate this t by z divide by U superficial velocity.

And, this term t which is written here is given in terms of z that is divide by U to the power 1 by 2. So, since U is superficial gas velocity and this case it is assumed constant. So, that has been taken here in A dash. So, this what t is equal to z divide by U where z is the height of the reactor and, U is the superficial gas velocity. So, this term which is a t to the power 1 by 2 and t is given by z upon U to the power 1 by 2 this term will come like this. And, A divide by U to the power 1 by 2 has been written here a dash times z to the power 1 by 2. So, if you look at or you combine your expression now here by substituting CA naught 1 minus xA. So, that expression has come now in this form dX by dz is equal to all other terms are mentioned as usual here times 1 minus x divide by 1 plus k is C naught 1 minus x times the phi which, is the deactivation function. So, one can very easily write either in terms of the bulk density or in terms of the volume of the reactor and volumetric feed rate.

So, this is how the deactivation function and the main rate reaction are correlated. So, one can design the reactor or one can find the conversion x for a given height. Or if, the conversion to be achieved is fixed then one can find out the height of the reactor when the catalyst is deactivating. So, this is a kind of that sizing a, reactor or design a reactor for the given system when the catalyst deactivation is significant because, of carbon formation. So, accordingly we have either the fluid catalytic cracking as I said that is fluidized bed reactor system or we can have a straight through transport reactor or which is a kind of moving bed reactor. So, catalyst are continually taken from bottom to the top and there activity is measured. And, then they are sent to a second column which is the regenerator and then recycled back into the system. So, that is known as straight through transport reactor or it is a kind of or simple moving bed reactor.

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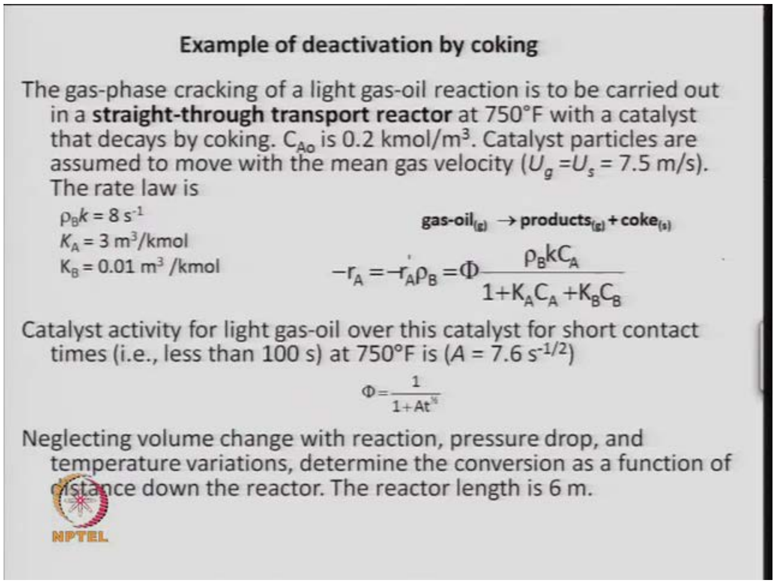

Example of deactivation by coking

The gas-phase cracking of a light gas-oil reaction is to be carried out in a **straight-through transport reactor** at 750°F with a catalyst that decays by coking. C_{Ao} is 0.2 kmol/m^3. Catalyst particles are assumed to move with the mean gas velocity ($U_g = U_s = 7.5$ m/s). The rate law is

$\rho_B k = 8\ s^{-1}$

$K_A = 3\ m^3/kmol$

$K_B = 0.01\ m^3\ /kmol$

$$\text{gas-oil}_{(g)} \rightarrow \text{products}_{(g)} + \text{coke}_{(s)}$$

$$-r_A = -r'_A \rho_B = \Phi \frac{\rho_B k C_A}{1 + K_A C_A + K_B C_B}$$

Catalyst activity for light gas-oil over this catalyst for short contact times (i.e., less than 100 s) at 750°F is ($A = 7.6\ s^{-1/2}$)

$$\Phi = \frac{1}{1 + At^{½}}$$

Neglecting volume change with reaction, pressure drop, and temperature variations, determine the conversion as a function of distance down the reactor. The reactor length is 6 m.

So, this is just as Example for practice so here if you look at the problem is something like that a gas is cracking of light gas oil is carried out in a straight through transport reactors.

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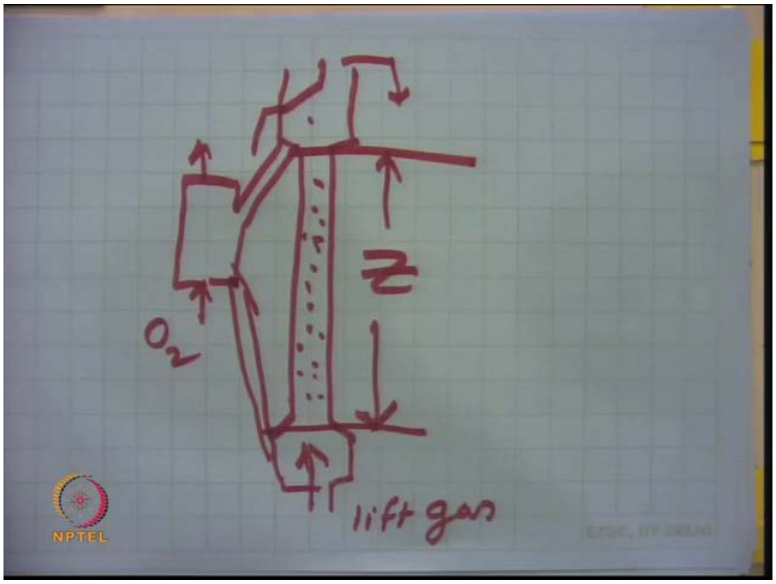

So, that what I was talking by straight through transport reactor is basically tube like this where you pass the feed from the bottom. So, feed is taken like this and it can be concurrent it can be count a current. So, feed along with the catalyst so catalyst particles are taken like this your catalyst particles are slightly larger compared to a fluidized bed reactor. In the case of fluidized bed reactor the baddish to be fluidized so, particles are smaller in size say 1micron to 50 micron 100 micron depends on the type of particles and the velocity. So, one needs stand here the particles can be larger say it can be 100 micron it can be 0.5 mm. So, one can take the accordingly and particles are moving on the bed like this. And, then you have a kind of reactor system here or a hopper system for the separation of the catalyst.

So, this in gaining hopper here so catalyst separates and the feed product goes here unrated feed products are taken in the separate unit. And, condensed and catalyst comes down here, and falls like this and comes into a reactor another reactor which is a regenerator basically. Where, oxygen is passed from the bottom or air is passed form the bottom. So, flue gas will go out like this and the catalyst is burned here and then regenerated and taken back into the system here by some lift gas so, need a lift gas here. So, this is a kind of some rough geometry of a moving bed reactor or also known as straight through transport reactor. So, different designers or different licenses are given different kind cal loge has 1 UOP has another one. So, different kind of designs are available for the hydrocarbon cracking. So, it can be atmospheric gas oil, vacuum gas oil naphtha all this so here this is what the height of the reactor to be decided in terms of the activity of the catalyst. So, one the catalyst comes here its activity drops so we are defining some kind of average activity. And, average conversion down the length of the tube or throughout the tube depending upon the superficial gas velocity. So, if you look at here the product the gas oil is to be carried out in a straight through transport reactor. And, temperature is given 750 degree for an height with catalyst that decays by coking.

So, deactivation of a catalyst is the because of the carbon deposition the concentration of the feed is given Ca naught 0.2 kilo mole meter cube. And, the catalyst particles are assume to move with a mean gas velocity which is given here Ug. And, that is constant here is equal to U as and that is equal to 7.5 meter per second rate law is given. So, kinetic rate constant K times row B is given 8second inverse. So, first tolerates constant KA is the equilibrium constant so 3meter cube per kilo mole and KB is for the product equilibrium constant. So, point 0.01 meter cube rater of reaction minus rA per unit volume of reactor is rA dash time row B. And, that is related to some deactivation function times your Langval Hinsellwood type mechanism.

So, rho B times kCA divide by 1 plus kCA plus kCB. So, this is a gas oil and converts to product so product may be gasoline gases everything and, plus the coke. So, phi the deactivation function which we have defined earlier also and given here by 1 divide by 1 plus At to the power 1 by 2 with A value is given 7.6 second inverse minus that is second to the power minus 1 by 2 neglecting the volume change during the reaction. So, epeplison is given 0 here and during no pressure of in the reactor determine the conversion as a function of distance down the reactor. So, one needs to find out the conversion as a function of z. So, that the expression d Xa by dz which I was talking earlier that is to be defined and here the value of z is given 6 meter.

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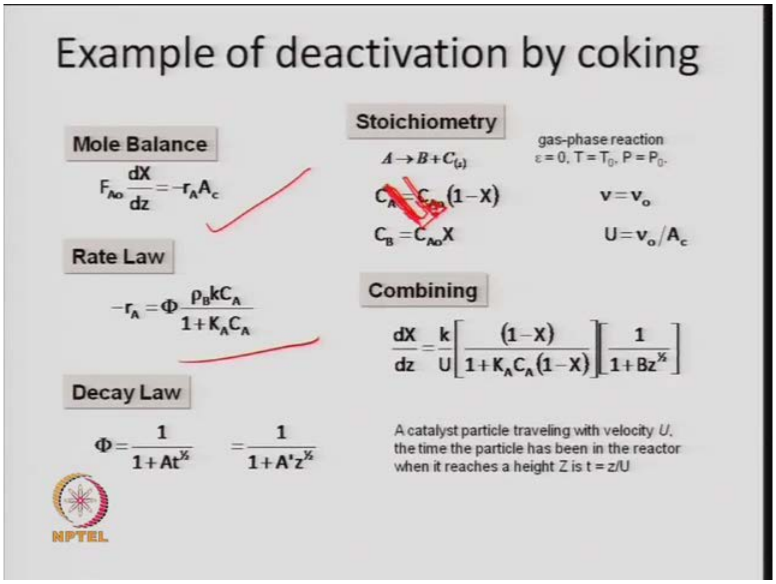

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Stoichiometry

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gas-phase reaction
$\varepsilon = 0$, $T = T_0$, $P = P_0$.

$$C_A = C_{Ao}(1-X) \qquad v = v_o$$

$$C_B = C_{Ao}X \qquad U = v_o/A_c$$

Combining

$$\frac{dX}{dz} = \frac{k}{U}\left[\frac{(1-X)}{1+K_A C_A(1-X)}\right]\left[\frac{1}{1+Bz^{½}}\right]$$

A catalyst particle traveling with velocity *U*, the time the particle has been in the reactor when it reaches a height Z is t = z/U

So, for a 6 meter long reactor the expression which we have defined like this the same is to be used here in terms of the deactivation function. So, that has been just discussed here so as a practice you need to check that and calculate. So, mole balance equation that is fA naught d Xa by dz is equal to minus rA into AC . So, one can write it in terms of the mass of the catalyst or in terms of the volume of the reactor. So, f A naught d Xa by dz is equal to minus rA into AC this is your mole valence equation rate law has been defined. So, that is minus rA equal to five times raho B times kCA divide by 1 plus kCA and one needs to identify this it can be 1 plus kCA plus kBCB also. So, that here we are assuming that this mechanism is already known and rate law is known to us. And, here the stoichiometry a gives you B plus C. So, B is your product and C is your carbon and CA is defined by CA naught 1 minus XA. So, that part we have already discussed earlier also.

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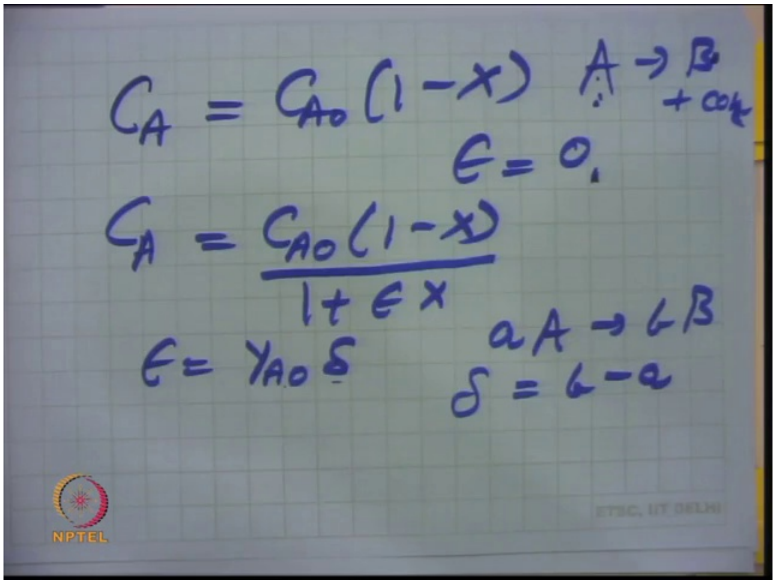

$C_A = C_{A0}(1-x)$ $A \rightarrow B + \text{coke}$

$\epsilon = 0.$

$C_A = \frac{C_{A0}(1-x)}{1+\epsilon x}$

$\epsilon = y_{A0}\delta$ $aA \rightarrow bB$

$\delta = b - a$

So, CA is equal to CA naught 1 minus XA because f epsilon is 0 if, there is f epsilon value then all of you know that CA is defined by CA naught 1 minus x divide by 1 plus epsilon x. Where, epsilon is the fractional change in volume. And, defined by YA naught into delta. So, YA naught is the mole fraction of the limiting component. And, delta is the change in a stoichiometry coefficient of the product and reactant. So, this is something like suppose small aA gives you a b moles of B then for this delta is simply b minus a. Or one can write it in terms of A is equal to B upon A times b.

So, epsilon will be that is Y naught is 1 in that case that depends on the mole fraction if inerts are added it will change. But, suppose if I say pure A is there then YA naught is 1and one can write with delta which is difference in the stoichiometry of this product minus reactant. So, one can define so in this case f epsilon is 0 same thing for CB because one mole of a gives you here by stoichiometry given like this plus coke, coke is a solid material so 1 mole of A gives you 1 mole of B. So, what about the moles of A reacted equal number of moles of B will form. So, fA naught is the inlet mole so fA naught 1 minus xA the moles of A which is left if you make this stoichiometry table. And, fA naught x is moles of A reacted. So, fA naught x of A moles of B will form. So, that is just the concentration of B in terms of the product which is written here CB is equal to CA naught x.

The volumetric florid as I said v is equal to v naught and U is superficial velocity v naught divide by the area of cross section of the reactor. So, one can very easily combine as I discussed so I am not going in detail of this so dxA by dz is equal to this equation which is simplification of this times 1 minus x divide by 1 plus kCA, which, is C naught 1 minus x time the deactivation function. So, this equation can be solved numerically to find out x as a function of z. So, one can use the met lab or polymer or the any kind of od can be used to solve this kind of equations. Which, are now the tools are available it possible one can solve it analytically also and one can plot the equations like this in this form.

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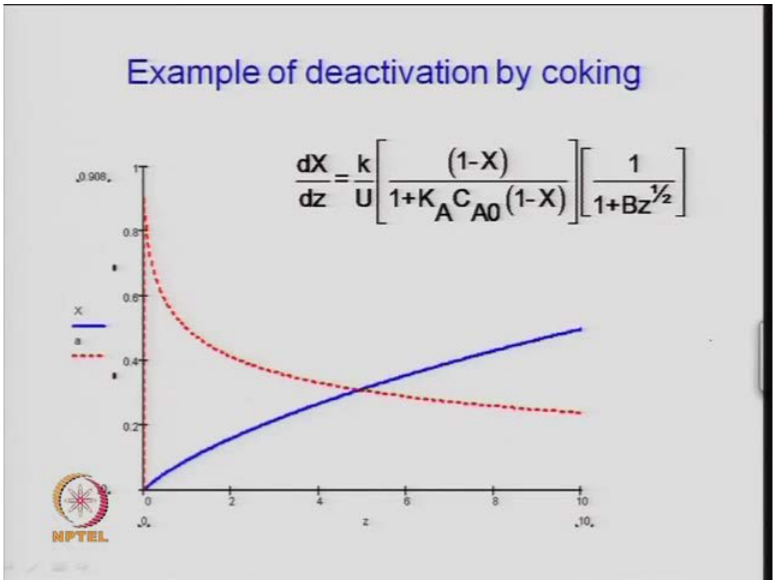

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$$\frac{dX}{dz} = \frac{k}{U}\left[\frac{(1-X)}{1+K_A C_{A0}(1-X)}\right]\left[\frac{1}{1+Bz^{1/2}}\right]$$

So, this is the activity profile which says that activity of the catalyst decrease with time on stream or as a function of z. So, here this time on a stream is up to the length of the reactor which is given here sh up to 6 meter here. But, one can have the profile to a different length also and one can decide that to what activity the reactor can be operated. That is mode of operation of the reactor till the catalyst deactivates or till activity reach to a level of the say 50 percent or 20 percent 30 percent it depends on the type of the reaction. So, here one can see for 6 meter the activity drops to a level of this which is roughly here say 0.35. So, one can write easily look at that and conversion this is increasing down the length of the reactor as you go up the conversion increased like this. So, one can plot the conversion or the activity as a function of time or the length of the reactor.

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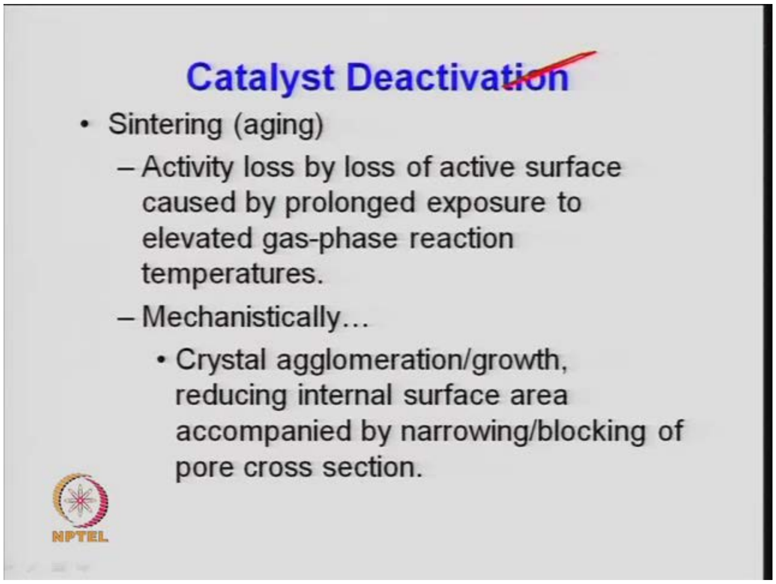

Catalyst Deactivation

- Sintering (aging)
  - Activity loss by loss of active surface caused by prolonged exposure to elevated gas-phase reaction temperatures.
  - Mechanistically…
    - Crystal agglomeration/growth, reducing internal surface area accompanied by narrowing/blocking of pore cross section.

So, this is what the Deactivation because of the coke formation what I discussed and because it blocks the active side. And, because of the blocking the active side or pore of a catalyst the rate of reaction decrease. So, one needs to reactivate or regenerate the catalyst by burning with oxygen and remove the carbon deposited on the catalyst to certain extent so, that the activity can be maintained. The, another kind of catalyst deactivation which I was talking is because of Sintering. So, Sintering is the loss of activity of a, catalyst caused by prolonged exposure to elevated gas phase reaction temperature. So, as I said that when the catalyst is continually exposed to a high temperature value, then the activity of the catalyst decrease because of the change in phase of the catalyst.

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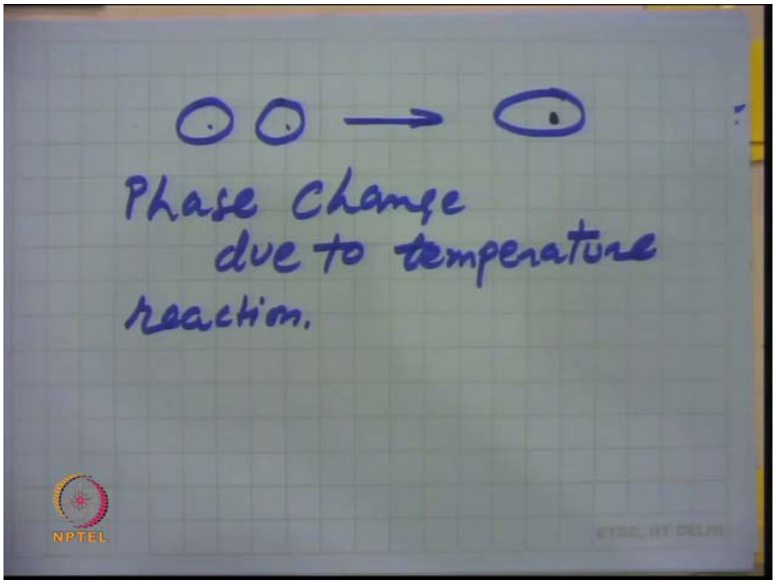

Phase Change
due to temperature
reaction.

So, it is something where the agglomeration takes place which I discussed earlier this because of this agglomeration the particles gets centered. And, this is nothing but a, grow of the crystal size. So, smaller crystals they agglomerated made a larger crystal so this is because of the centering and this sometimes reduces the pore size of the catalyst. And, also there is a Phase Change due to temperature reaction I will say because high temperature reaction solid material they react together or nickel react with alumina say and form nickel aluminate. So, this is a kind of phase change and therefore the activity of the catalyst decrease during the course of reaction.

So, mechanistically if you see here the crystal agglomeration or growth of the crystal reducing the internal surface area accompanied by narrowing or blocking the core of a cross section. So, that is again very common phenomenon especially when the catalyst is treated at high temperature. High temperature say zeolite catalyst zeolite catalyst cannot sustain temperature more than 550 or 600 degree centigrade. So, if the reaction is required higher temperature then one needs to stabilize the catalyst. So, that this should not agglomerate or the active sides of the catalyst should not grow if you need especially smaller particle size during the reaction. So, that becomes very important when you look at the deactivation phenomenon and especially where the phase change. So, because of the height temperature and time the there is a kind of solid reaction between the metal and the support and the get transformed to different phase and that decrease the activity of catalyst. So, one simple example say in the case of fishiotope reaction the iron or nickel they form some kind of nickel carbonyl iron carbide. But, some times the particular phase nickel carbonyl say it may not desired of the reaction or iron carbonyl may not be desired so that drops the activity of the catalyst.

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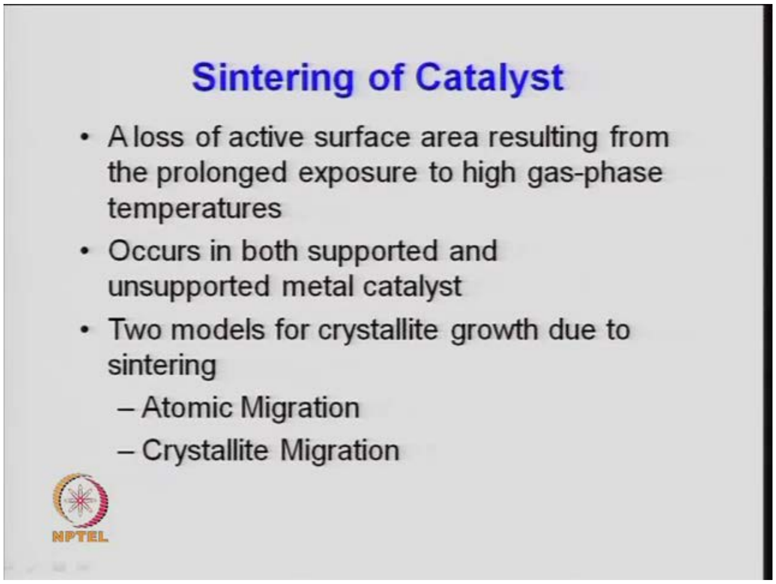

Sintering of Catalyst

- A loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures
- Occurs in both supported and unsupported metal catalyst
- Two models for crystallite growth due to sintering
  - Atomic Migration
  - Crystallite Migration

So, loss an active surface area which results from prolonged exposure to high gas temperature that is undesired and occurs in both supported and unsupported metal catalyst. So, when you have a, nano particles so they will get agglomerated and activity will drop. So, if that is what I said that nano partial preparation may not be too difficult but to make the mist able during the catalytic reaction especially when the temperature is high that is a difficult to tds job. So, two models are generally here used in terms of the crystal growth because of the sintering one is known as Atomic Migration where atoms migrate.

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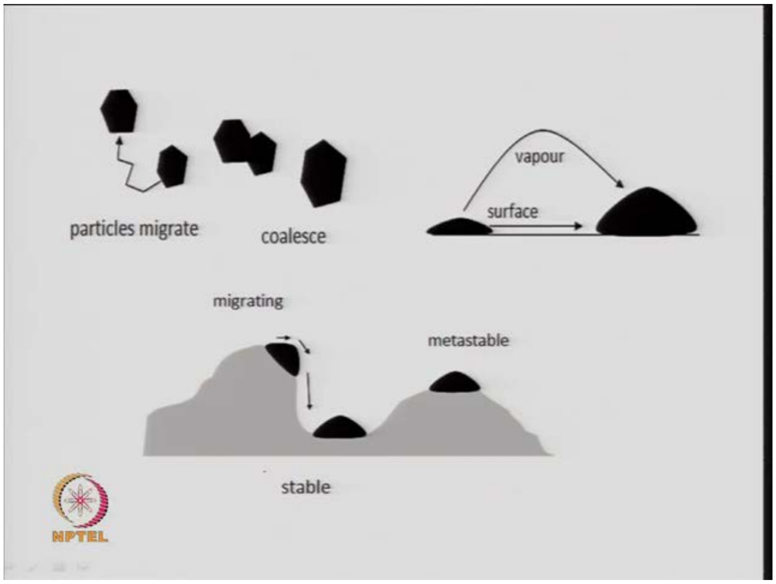

And, second is the Crystal Migration where the total crystallite which form during the reaction they migrate and it may be through surface diffusion, which is something like here the particles if you look at here these two particles they migrate when the surface because of the temperature time and they get agglomerated form a larger. So, this is what they coalesce here. So, the crystal grows inside and same thing is the here the surface or through the gas phase so, they migrate and get agglomerated and this is the sintering. So, reduction can be defined or activity of a catalyst can be correlated by decrease in surface area of the catalyst per unit mass of a catalyst. And, same thing here the they get migrate here and they come here. And, so this is kind of migrating molecule they come in the stable form like this metastable. So, they migrate and they get again agglomerated and they move to the pore and they block the pore. So, all kind of mechanism may be possible during this sintering.

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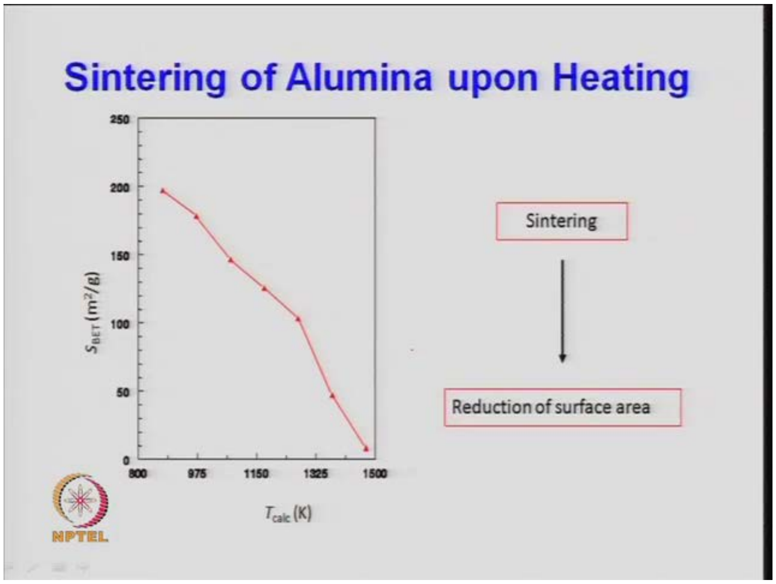

Sintering of Alumina upon Heating

Sintering

Reduction of surface area

And, consequences of Sintering just for an example if you take Alumina support and no metal part even there are no metal part the surface area of the alumina. If, you look at around 850 degree centigrade Calvin. So, it is roughly 190 meter square per gram but when you give the temperature treatment or you heat it to different temperature range. Then, the surface area change because the phase transformation or the agglomeration. So, it is a pores material and here it becomes a kind of non pores material a kind of alpha alumina which you get here and this may be a kind of gama alumina here.

So, that is what I told that there is a kind of change of phase or there is a kind of change of the structure of the crystallites. So, there is the decrease in the surface area of the catalyst. When, the surface area is less your active sides will reduce accordingly. Or, preparation when you do the catalyst preparation it become difficult And, finally the agglomeration of the pore because of the low pore volume or low surface area and overall rate of reaction will decrease because of this phenomena.

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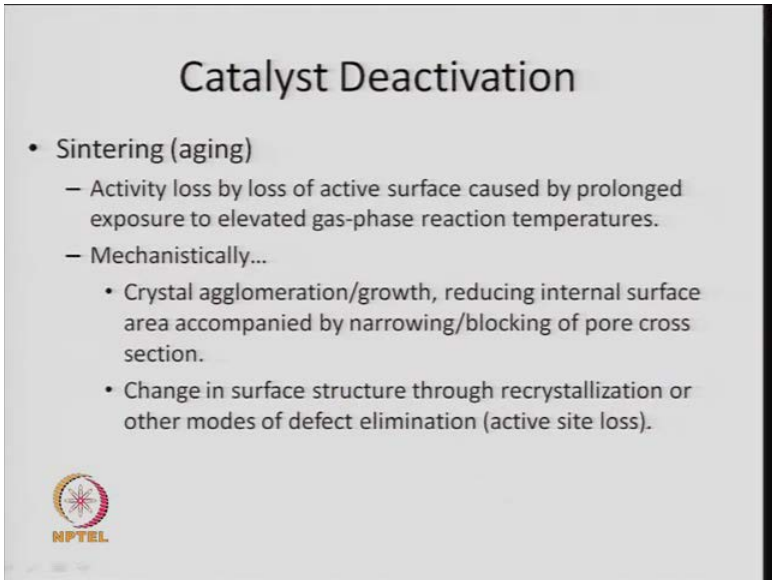

Catalyst Deactivation

- Sintering (aging)
  - Activity loss by loss of active surface caused by prolonged exposure to elevated gas-phase reaction temperatures.
  - Mechanistically…
    - Crystal agglomeration/growth, reducing internal surface area accompanied by narrowing/blocking of pore cross section.
    - Change in surface structure through recrystallization or other modes of defect elimination (active site loss).

So, it is a kind of aging because temperature time relation for how much time and how much at how much temperature the catalyst has been in contact. That, environment of high temperature and time so the activity loss or loss of active sides which are discussed and, because of the agglomeration, so that kind of mechanism although the details are not available and lot of r and d may be done to understand for a, given catalyst for a given support material. And, how do they agglomerate that is how the crystal size grow or when nano particles how do they grow during the temperature time treatment and one can identify the mechanism and find a solution for that in order to reduce. So, catalyst the promoters can be added to reduce that crystallite just like as an example if you have the iron catalyst or a kind of say cobalt catalyst.

So, if you add some kind of copper promoter. So, copper comes in between the two iron particles then prevents the agglomeration to some extent either copper or that is either co cobalt or iron. Which, are generally used for the fishotrope reaction. So, there are different kind of promoters can be added to enhance or to improve the stability of the catalyst which is because of the sintering phenomenon. So, in the case of commercial reactors if you look at the activity of catalyst is decrease with time on stream. So, generally the obscene are either you regenerate the catalyst or second option can be that increase the temperature. Because, the rate of reaction will increase or your rate constant will increase when temperature is increased and in order to compensate the drop decrease in activity of a catalyst that can be compensated by increasing the temperature. So, that part I will take little later. But, if you look at the deactivation mechanism because of sintering so just like in the case of poisoning or falling we have discussed. That, the activity drops as a function some deactivation function some.

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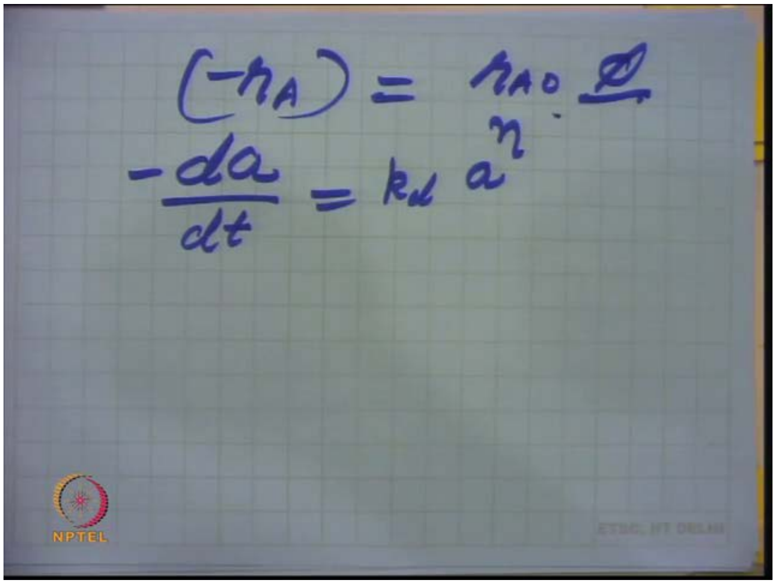

$$(-r_A) = r_{A0} \cdot \underline{\phi}$$

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

So, minus da by dt all the time but we write here is something times kd times the activity to the power n something like that. Where a is a kind of activity function or this whole thing can be written in terms of the when I write rate minus rA can be written in terms of rA 0 times some function of this which can be calculated from this. So, this basically activity of a catalyst and how does it drop will depend on the mechanism of the catalytic reaction.

So, this drop in activity as I said may be because of falling may be because of poisoning or may be because of sintering. So this similar expressions that is that deactivation order which I was discussing here n and the rate of deactivation that is kinetics of deactivation if you look at that can again be discussed just like kinetics of the main chemical reaction. That, is first order deactivation, second order deactivation or any nth order deactivation. And, these can be find out just by the same method like first differential method of analysis or entriogal method of analysis. So, same reactor that is the catalytic reactors which are generally used for screening small in the differential form they can be used to determine the deactivation function during a catalytic reaction. Or, when we screen out the catalyst then activity of a catalyst can be measured for different cattily. So, this n is a kind of order of deactivation and this can be find out by assuming say first order deactivation or second order deactivation.

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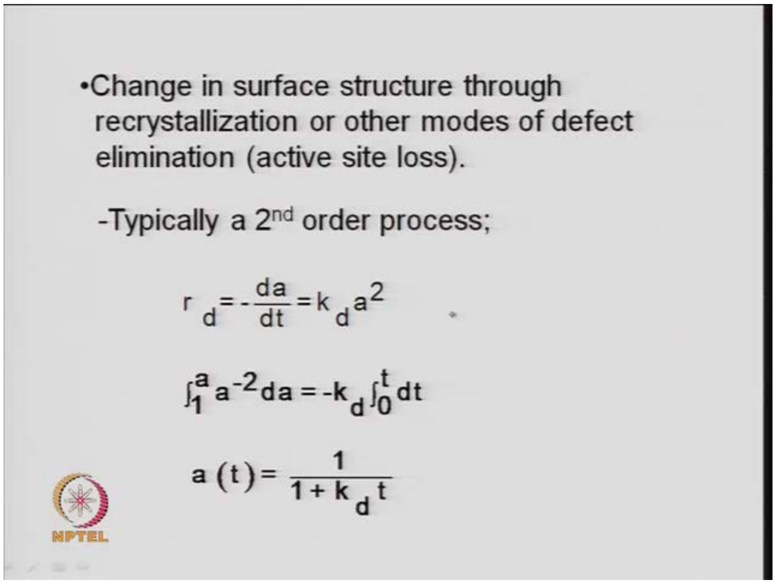

- Change in surface structure through recrystallization or other modes of defect elimination (active site loss).

  -Typically a 2nd order process;

$$r_d = -\frac{da}{dt} = k_d a^2$$

$$\int_1^a a^{-2} da = -k_d \int_0^t dt$$

$$a(t) = \frac{1}{1 + k_d t}$$

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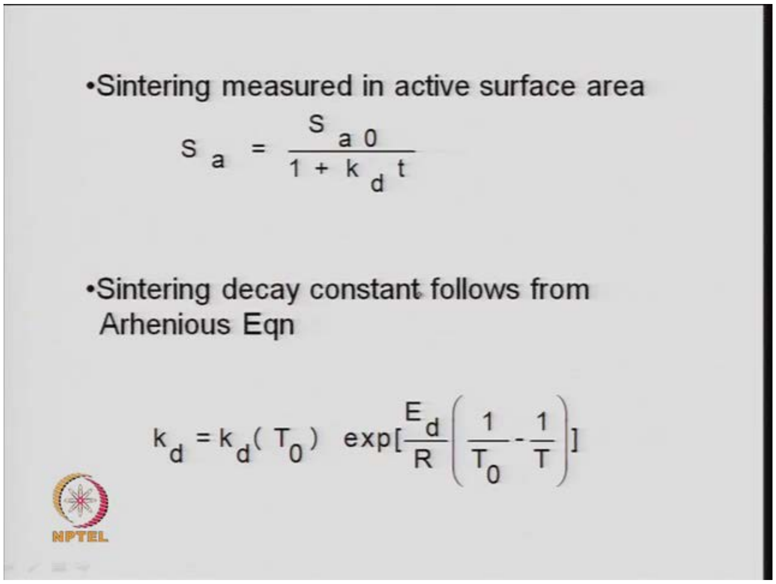

- Sintering measured in active surface area

$$S_a = \frac{S_{a0}}{1 + k_d t}$$

- Sintering decay constant follows from Arhenious Eqn

$$k_d = k_d(T_0) \ \exp\left[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

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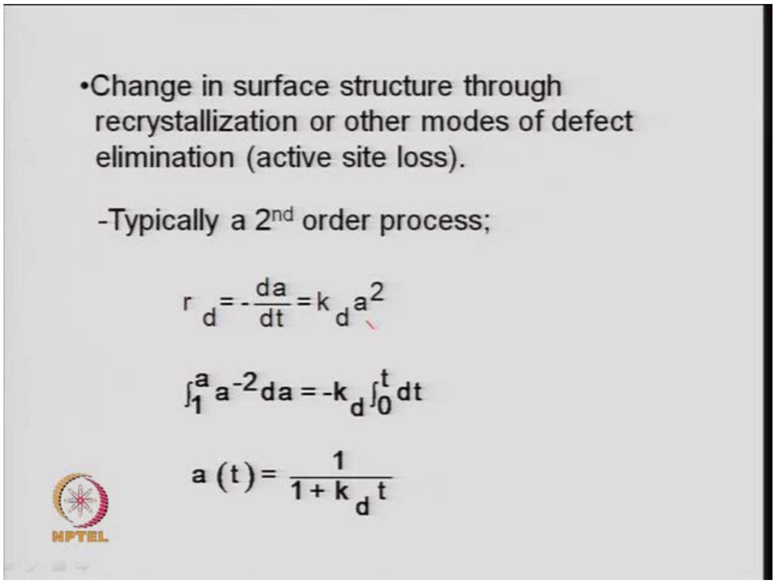

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So, in the case of sintering generally it is assumed as a second order deactivation so that can be correlated like this. So, minus rd which is the rate of deactivation is equal to minus da rd is the rate of deactivation is related to minus da by dt that is decrease in activity with time. And, that is related to kd times a square which is for the second order deactivation so, this is a second order deactivation. And, now one can interrogate because by separating the variables so minus da divide by a square is equal to kd t which is written here. So, da divided by a square is equal to kd times 0 to t dt. And, how the limit will change because when the catalyst is fresh the activity is one because activity you define rate at any time divide by rate when the catalyst was fresh. So, at t is equal to 0 the catalyst is fresh so rate rA and rA 0 are same. So, your activity for a fresh catalyst will be 1 so for t is equal to 0 activity is 1 and at any time t the activity drops to value a. So, one can interrogate this expression and the simply d upon a square and here it is minus 0 to t.

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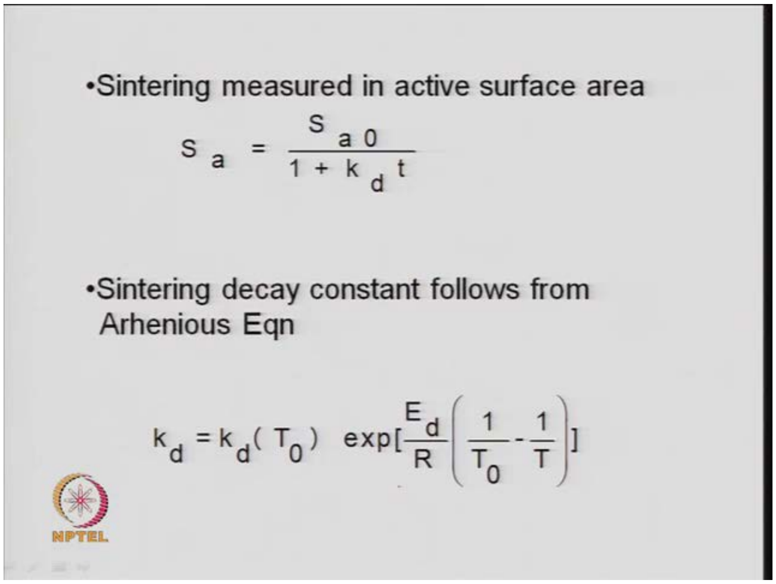

- Sintering measured in active surface area

$$S_a = \frac{S_{a0}}{1 + k_d t}$$

- Sintering decay constant follows from Arhenious Eqn

$$k_d = k_d(T_0)\ \exp[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)]$$

So, the this is simply time one can write the expression if you interrogate this by substitution the limit so at is equal to 1 over 1 plus kd t. So, this is a kind of expression for deactivation because of sintering on especially what I am saying in general a second order deactivation. So, this just say is that the activity of the catalyst will drop with time on stream. And, in other words I can correlate it with surface area of a catalyst. So, initial because sintering means both of the particle so, because of that surface area of the catalyst decrease so in that case how surface area decrease because of the time on a stream. And, that is correlated with the activity of a catalyst so one can correlate s a which is surface area at any time T just like the rate at time is nothing but initial surface area multiplied by the activity of a catalyst and that we have already defined here.

So, this is simple S is 0 which is the surface area of the fresh catalyst n times this deactivation function which is one divide by one plus kd t for second order deactivation. So, one can write the expression for different type of deactivation functions. So, sintering equation if you look at with time on stream again this whatever, the kd which we are writing that is related to temperature. So, one can write kd is equal to kd at t0 which is at some refresh temperature times exponents of ed. Which, is the activation energy for the deactivation reaction divide by the gas constant times 1 by t0 minus 1 by t. So, this is the kd calculated at any temperature t, so why do we need this because as I said that some times in order to compensate decrease in activity can be done by increasing the temperature. So, although when you increase the temperature the deactivation rate constant will also increase and rate constant for the main reaction will also increase.

So, depending upon the activation energy or the deactivation reaction and main reaction which we will talk little later and one can see how much temperature should be increased or how mush temperature is to be increased in order to compensate the decrease in activity of the catalyst. So, that is very important especially when the activity drop faster and regeneration is not possible say in that case of kind of fix bed reactor the regeneration of catalyst may be difficult. So, in order to maintain the activity the temperature so after 6 months of operation the temperature can be increased by 10 degree centigrade or 50 degree centigrade to a maximum whatever the formation will limit in order to get the higher productivity.

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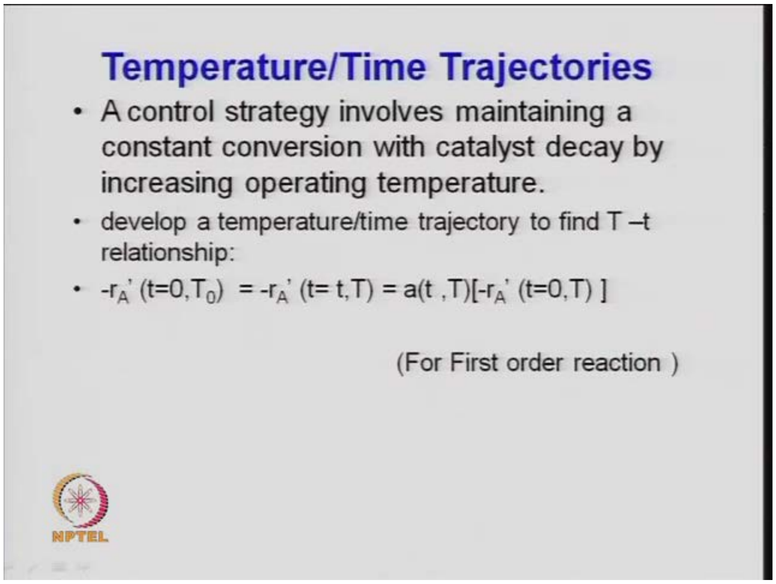

Temperature/Time Trajectories

- A control strategy involves maintaining a constant conversion with catalyst decay by increasing operating temperature.
- develop a temperature/time trajectory to find T –t relationship:
- $-r_A'\ (t=0,T_0) = -r_A'\ (t=t,T) = a(t,T)[-r_A'\ (t=0,T)]$

(For First order reaction)

And, this is what I was talking how to look at that how to find out that how much temperature is to be increased you need to find out a Temperature Time Trajectories. So, this is important if not then the catalyst deactivation is fast very fast just like as I said the catalyst deactivates continuously. And, when you have a food catalytic cracking or moving bed reactor this kind of temperature time trajectory may not be effective. So, this effective only when the deactivation is slow or activity drops at a slower rate sop in order to maintain the activity one can increase the temperature after certain time or one can have the temperature time trajectory something like this t versos times.

So, what is the meaning of temperature time trajectory it is simply where it is an controlled strategy which involves maintaining a constant conversion with catalyst dk by increasing the operating temperature. So, develop a temperature time trajectory and this simply says that if you know the rate at any time t. Which, is lower because rate at any time T will be related to the rate at t is equal to 0 multiplied by the activity of a catalyst which we have already discussed. And, this activity of a catalyst decrease with time on stream. So, if somehow we know that how this activity decrease with time that is a deactivation function is known. Then, one can increase the temperature accordingly because when you increase the temperature then rate constant will increase from Arrhenius law RNS law equation. So, it means this r a at any time t will be now rA at some higher temperature T.

So, what we have done that whatever the drop in this activity with time has been compensated by increasing this value by increasing the temperature at that time. So, How much temperature is to be increased? That, can be correlated by using the Arrhenius law equation so that as I said the temperature will affect the deactivation rate constant as well as the rate constant for the main reaction also but, one can correlate these two. So, look at here that k at n temperature t which is the rate constant for the main reaction will be related to the activity because this expression. So, rA which is written here rA dash at tn time is nothing but activity multiplied by that time and temperature time the rate constant for the main reaction and that is equated to the rate when the catalyst was fresh. So, concentration is same the relation is made now with respect to Arrhenius law expression which is now rate constant evaluated at t0 temperature t0. So, this is a kind of re parameterization so this is not the ((Refer Time: 40:14)) this is the rate constant measured at some refresh temperature t0.

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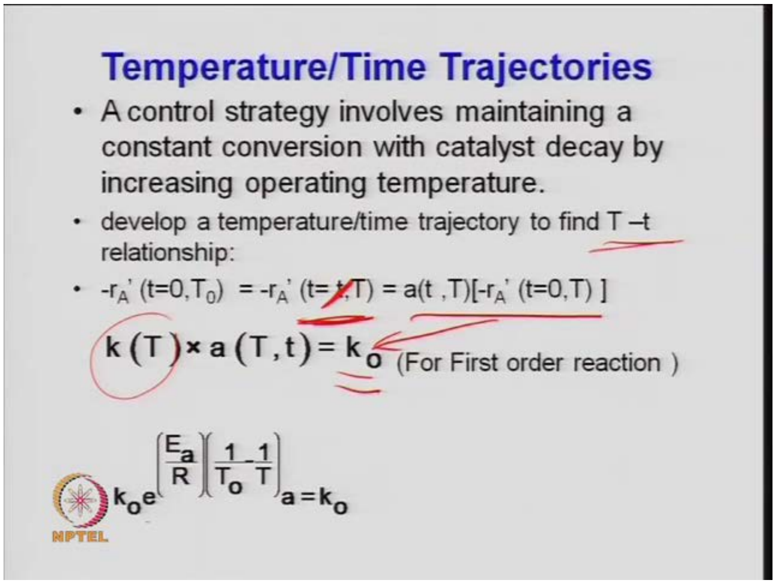

Temperature/Time Trajectories

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- develop a temperature/time trajectory to find T –t relationship:
- $-r_A'(t=0,T_0) = -r_A'(t=t,T) = a(t,T)[-r_A'(t=0,T)]$

$$k(T) \times a(T,t) = k_o \text{ (For First order reaction)}$$

$$k_o e^{\left(\frac{E_a}{R}\right)\left(\frac{1}{T_o}-\frac{1}{T}\right)} a = k_o$$

So, one can write this because K you know from Arrhenius law equation K0 E to the power minus E upon RT that is Arrhenius law equation. But, when I am writing k1 by k2 so that is represent this is the now rate constant measured at temperature t0. So this is rate constant measured at temperature t 0 times E to the power e upon r1 by t0 minus 1 by T. And, that is equated to the initial rate that is when the temperature is t0.

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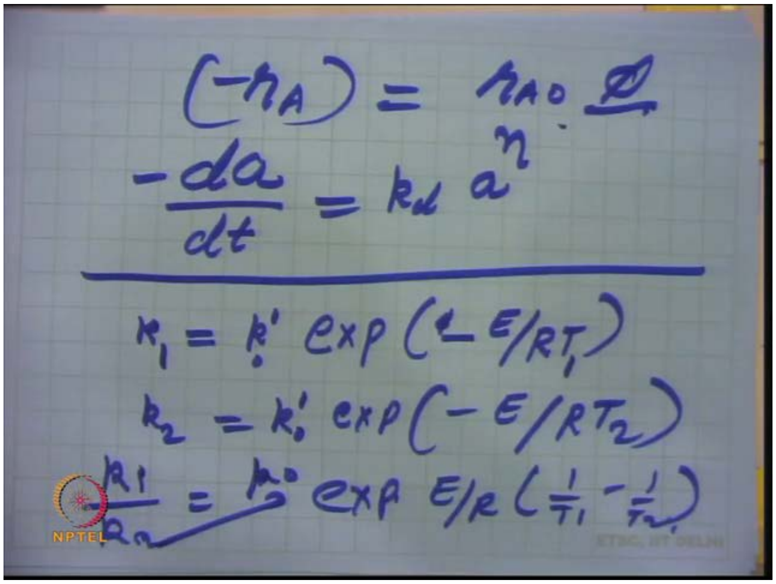

$$(-r_A) = r_{A0} \cdot a$$

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

$$k_1 = k_0' \exp(-E/RT_1)$$

$$k_2 = k_0' \exp(-E/RT_2)$$

$$\frac{k_1}{k_2} = k_0 \exp E/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

So, what is done here if you try to correlate so rate constant generally you define k is equal to some pre exponential factor which is k0 dash e to the power minus E divide by RT. Where, E is the activation for the reaction and T is the temperature in Kelvin. So, if I write rate constant at two temperature k1 this is T1 and another temperature k2 this is again k0 dash exp minus E divide by RT 2. So, this now here in this case what we have done t0 has been taken as a refresh temperature. And, t at any temperature we have illuminated these two so k31 divide by k2 is equal to this cancels when you take the ratio.

So, exp minus e upon r1 by T2 minus 1 by T1 or 1 can write it in this form. So, this is what expression calculated in the form of k1 by k2. So, which is, just now exp, and that will be defined in terms E upon R 1 by T1 minus 1 by T2 something like this T1 is here t0 here. And, T2 is any temperature t so this k two will become your k0 here in this case we have written this as a refresh temperature. So, this will be basically in the form of this k1 is your now any temperature t and k2 I have taken here as a refresher or one can write in terms of the ratio k2 by k1that time you will get the expression similar to that. So, basically exp minus E upon R you take out so this is simply one by T2 minus one by t one so that is what one can simplify.

So, this is the expression which is written here and now if you use this expression you can very easily find out because k0 cancels. So, one can write the expression for activity from this equation this one is equal to e to the power E upon R E a upon R where Ea is the activation energy for the main reaction 1 by t0 minus 1 by t. So, one can write from this if you take log so this times log of a equal to whatever the expression here written in the form of 1 by t. So, one can write it 1 by T minus 1 by T0 is equal to simply R upon Ea lna. This, is from this equation 1upon t or 1upon T minus1 by T0. So, I have taken it other side so R upon E times ln of a. So, that is the expression how temperature and activity are correlated if, this is known at temperature T0. So, activation at for the main reaction is known from the kinetics and one can find out what is the activity as a function of temperature. And, once this activity is known this can be substituted in the deactivation equation.

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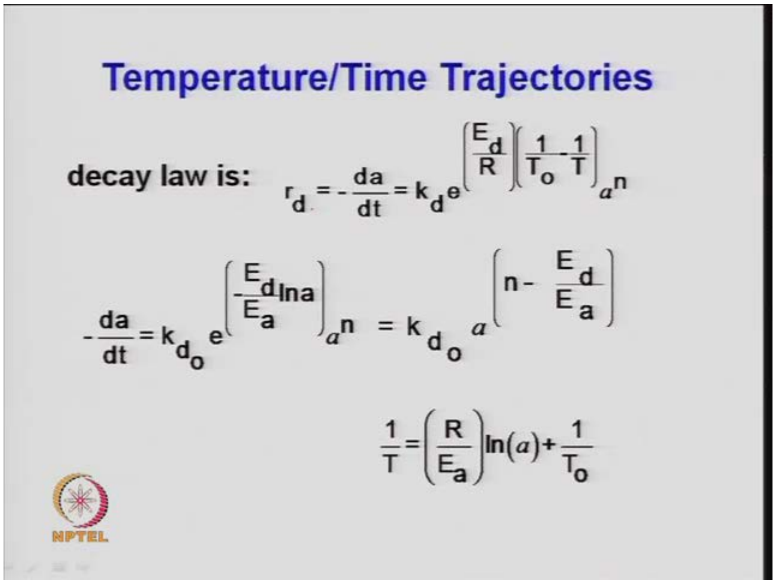

Temperature/Time Trajectories

decay law is: $r_d = -\frac{da}{dt} = k_d e^{\left(\frac{E_d}{R}\right)\left(\frac{1}{T_o}-\frac{1}{T}\right)} a^n$

$$-\frac{da}{dt} = k_{d_o} e^{\left(-\frac{E_d \ln a}{E_a}\right)} a^n = k_{d_o} a^{\left(n-\frac{E_d}{E_a}\right)}$$

$$\frac{1}{T} = \left(\frac{R}{E_a}\right)\ln(a) + \frac{1}{T_o}$$

So, this your dk law so your rate of deactivation or the rate for the deactivation is related to the activity. So, rd is minus da by d T that is equal to kd times again it is related with the Arrhenius constant. So, kd is at refresh temperature that is measured at temperature T0 times E to the power minus EdE to the power Ed upon r now times one by T0 minus 1 by T and, times a to the power of n.

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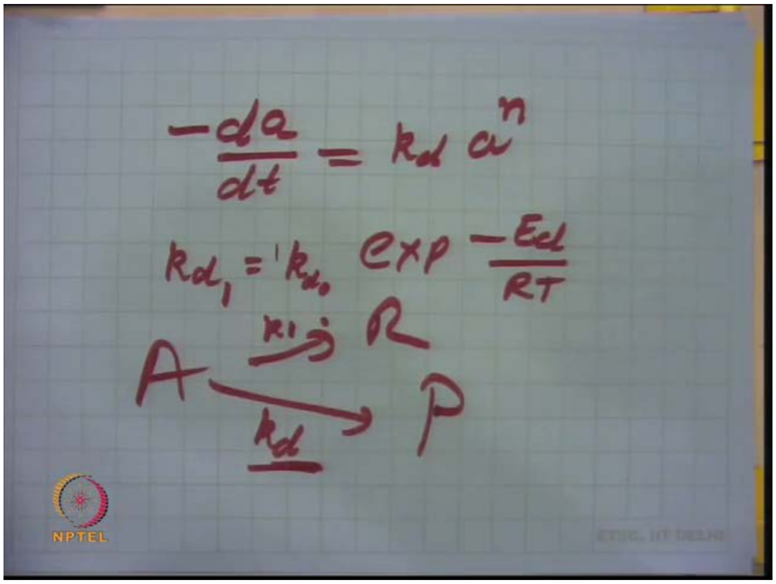

$$-\frac{da}{dt} = k_d a^n$$

$$k_{d_1} = k_{d_0} \exp -\frac{E_d}{RT}$$

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow[\underline{k_d}]{} P$$

So, basically we have written our deactivation equation minus da by dt is equal to kd times a to the power n. And, kd can be correlated just for Arrhenius equation is 0 first I will writ here which is per exponential factor times exp minus Ed divide by RT that is the expression which is written here. And, again as usual done in the earlier case so we are calculating the ratio kd1 and kd2. So, kd2 divide by kd1 just like because at temperature T1 there is some constant deactivation constant and at T0 there is some deactivation constant.

And, these because Arrhenius equation will tell how the rate constant increase with temperature. So, rate constant for the main reaction is also increasing and for deactivation it will also increase. So, for both main as well as the deactivation reaction the rate will increase. So, this is something like A gives you R and A gives you kind of poison precursor here we are correlating it with the sintering. So, this is also increasing rate constant and this is for deactivation reaction and this is also increasing. So, one can correlate say one thing from so what is the activation energy for this reaction what is the activation energy for this reaction and you can see the relationship between the rates or if I just look at the desired product divided by undesired product one can find out from that also.

So, this rd which we defined, so now we can substitute the value of the activity here, from original equation which is from the main rate, so da by dt is equal to kd0 which is written now in terms of that temperature time relationship which we have defined temperature activity relationship. So, kd0 e to the power Ed upon Ea ln of a times a to the power n and that becomes if you simplify this equation this becomes kd0 a to which is here combined term. So, this E to the power Ed upon a so I can write it ln of Ed upon Ea to the power a to the power E Ed upon Ea negative sign and this now has the same unit so one can just take it together. So, n minus Ed so this is n here and this is minus Ed upon Ea so this can be written in terms of power hereSo, this expression which this kd has been replaced from here which is your original equation here so we substituted the value of activity.

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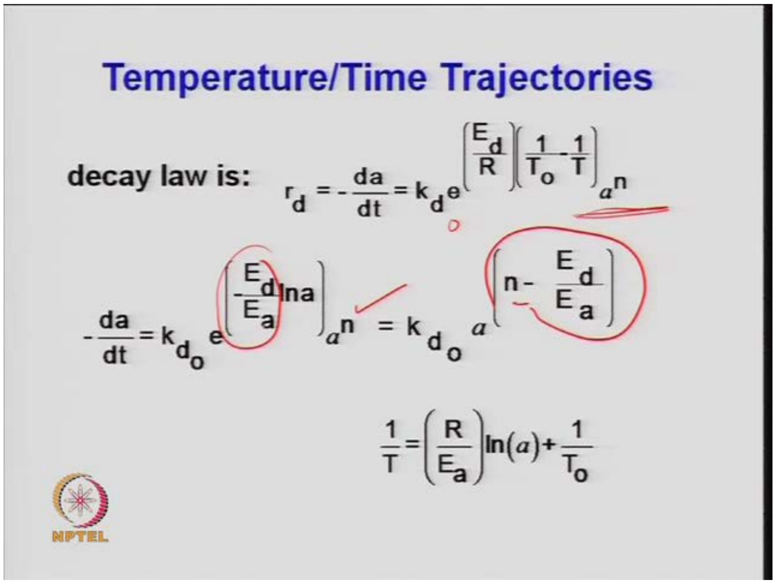

Temperature/Time Trajectories

decay law is: $r_d = -\frac{da}{dt} = k_{d_o} e^{\left(\frac{E_d}{R}\right)\left(\frac{1}{T_o}-\frac{1}{T}\right)} a^n$

$$-\frac{da}{dt} = k_{d_o} e^{\left(-\frac{E_d}{E_a}\ln a\right)} a^n = k_{d_o} a^{\left(n-\frac{E_d}{E_a}\right)}$$

$$\frac{1}{T} = \left(\frac{R}{E_a}\right)\ln(a) + \frac{1}{T_o}$$

So or in one way you can say substitute the value of 1 upon T minus 1 upon T0 that is equal to R upon Ea ln of a from this equation the value is substituted here. So, 1 upon T0 minus 1 by T and that has been changed to R upon. So, which is cancels now because this R that R gets canceled. So, finally you have minus E d upon Ea and Ea upon Ed upon Ea ln of a so that can be written in terms of the power form. So, kd0 a to the power n minus Ed upon Ea we get.

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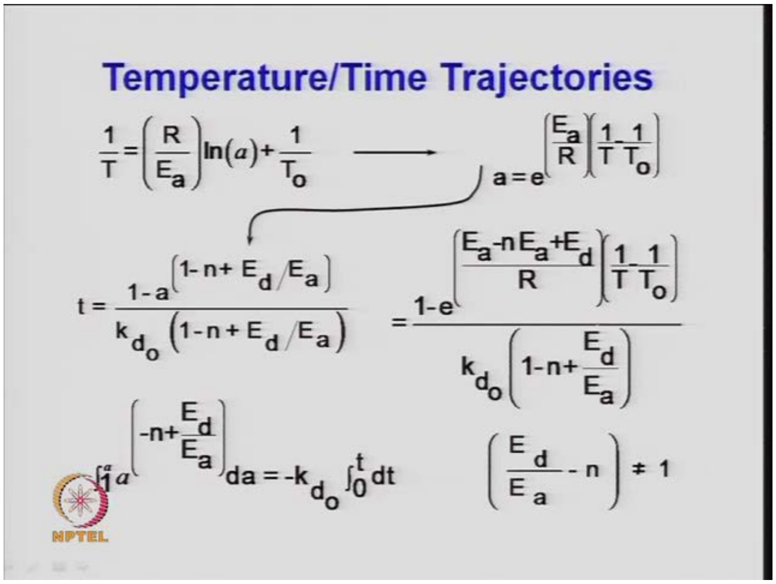

Temperature/Time Trajectories

$$\frac{1}{T} = \left(\frac{R}{E_a}\right)\ln(a) + \frac{1}{T_o} \longrightarrow a = e^{\left(\frac{E_a}{R}\right)\left(\frac{1}{T}-\frac{1}{T_o}\right)}$$

$$t = \frac{1-a^{\left(1-n+E_d/E_a\right)}}{k_{d_o}\left(1-n+E_d/E_a\right)} = \frac{1-e^{\left[\frac{E_a-nE_a+E_d}{R}\right]\left(\frac{1}{T}-\frac{1}{T_o}\right)}}{k_{d_o}\left(1-n+\frac{E_d}{E_a}\right)}$$

$$\int_1^a a^{\left[-n+\frac{E_d}{E_a}\right]} da = -k_{d_o}\int_0^t dt \qquad \left(\frac{E_d}{E_a}-n\right) \neq 1$$

So, once this is known now the integration can be done for the expression. So, because you have already obtained this relationship temperature versos activity that is 1 the expression for activity is now related aE to the power ER1 by t minus 1 by T0. So, minus Ra which is Rd is equal to minus da by dt is equal to kd to the power n. So, one can impregnate because now activity is known in this form your original equation. So, integrate this equation for the limit again as usual that t is equal to 0 activity is 1 n to any time a at any time t activity is a. So, one can impregnate this expression and find out the time for achieving a given activity.

So, that is a it is something like that after time 6 months say what is the activity of a catalyst, which is correlated with temperature now that is how much because it will depend on Ed upon Ea value that is activation energy for the deactivation reaction and activation energy for the main reaction and order of reaction. Suppose, n is 1 so this is just a to the power Ed upon Ea so one can very easily find out whether deactivation activation is for deactivation reaction is higher or main reaction is higher. And, accordingly after how much time the activity will drop to some value 50 percent say 8.5.

So how much is the time? So, one can find out because all other terms are known now was the mechanism of the main reaction and mechanism of the deactivation reaction is more. So, one can very easily substitute this expression in other form and get the expression in terms of temperature and time. So, this is what the integration has been shown here 1 2 a a to the power minus n times Ed upon Ea which is this expression da and that is equal to other side minus kd0 0 to t dt because this is your Rd is equal to minus da by dt is equal to kd times a to the power n and that is the expression which has been integrated to find out this time. So, one can calculate this and the only limit here is that E d upon Ea minus n should not be equal to 1 otherwise it will be in determinant form.

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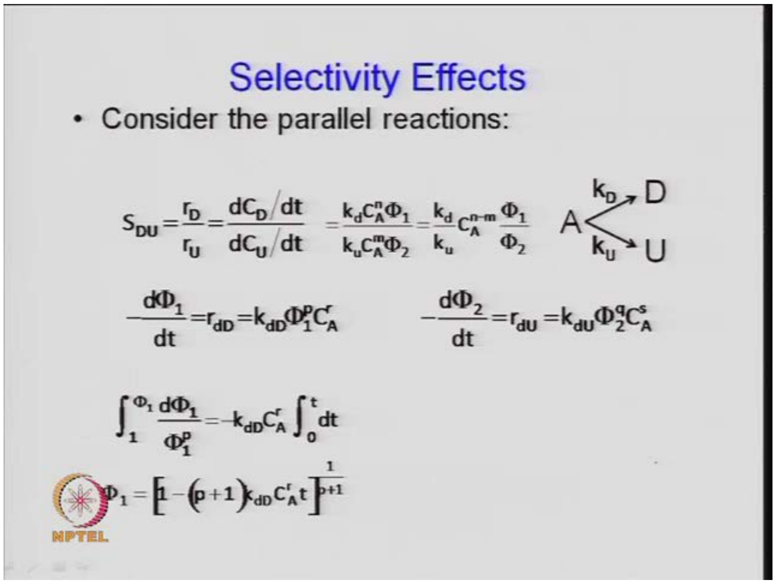

Selectivity Effects

- Consider the parallel reactions:

$$S_{DU}=\frac{r_D}{r_U}=\frac{dC_D/dt}{dC_U/dt}=\frac{k_d C_A^n \Phi_1}{k_u C_A^m \Phi_2}=\frac{k_d}{k_u}C_A^{n-m}\frac{\Phi_1}{\Phi_2} \qquad A \begin{cases} \xrightarrow{k_D} D \\ \xrightarrow{k_U} U \end{cases}$$

$$-\frac{d\Phi_1}{dt}=r_{dD}=k_{dD}\Phi_1^p C_A^r \qquad -\frac{d\Phi_2}{dt}=r_{dU}=k_{dU}\Phi_2^q C_A^s$$

$$\int_1^{\Phi_1}\frac{d\Phi_1}{\Phi_1^p}=-k_{dD}C_A^r\int_0^t dt$$

$$\Phi_1=\left[1-(p+1)k_{dD}C_A^r t\right]^{\frac{1}{p+1}}$$

Same thing for the selectivity also because the when there is a deactivation the catalyst activity is decreasing and because of that selectivity may also be affected. So, there are different infusion diffusion instant may also have influence so that we will see little later that depends on the time permitting. So, this expression which is on Selectivity Effect that if you look at just an example we have considered parallel reaction here A gives you the desired product DA gives you undesired product U. So, How do you define selectivity and yield? So, generally yield we define

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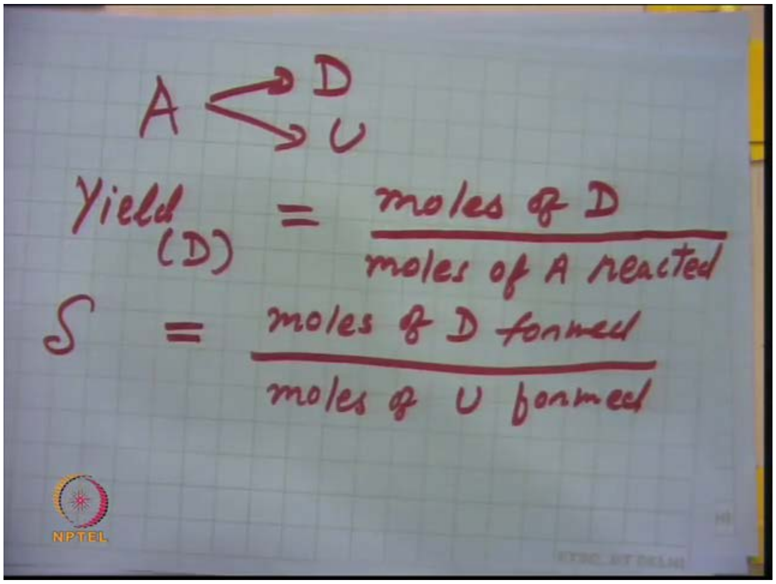

$$A \begin{cases} \to D \\ \to U \end{cases}$$

$$\text{Yield}_{(D)} = \frac{\text{moles of D}}{\text{moles of A reacted}}$$

$$S = \frac{\text{moles of D formed}}{\text{moles of U formed}}$$

Suppose, the reaction gives here given here is D and U so D is the desired product U is the undesired product so yield of D. So, yield generally defined for the desire product so moles or mass of the desired product D produced divide by moles of A reacted so this is the definition of yield. But, the more important thing here is that selectivity so selectivity which is defined here in terms of desired product to the undesired product, so S or D will be defined moles of D produced divide by moles of U produced or formed.

 So what is our aim? We, have to maximize this D form per unit moles of U form. And, that is again a function of your temperature time relationship because of deactivation rate of formation of this will be different rate of formation of this will be different and deactivation minus DA by dt that is A1 for this will be different and minus DA 2 by dt for this will be different. The order of deactivations may be different deactivation kinetics may be different. So, it mean it will depend on overall mechanism of the main reaction as well as the mechanism of the deactivation reaction. And, objective will be how to maximize this selectivity. So here just, as a example if you look at the selectivity with respect to U D U which is defined Rd divided by RU that is the moles or mass of the D produced rate of production of D divide by rate of production of U.

So, that is defined by dCd by dt divide by dCu by dt which is rate and this rate is formation is in terms of related to the some function of the main reaction so rate constant for D this is not deactivation the rate constant for D times kCA power n. So, we are writing minus rA is equal to kCA to the power n. So, this the main reaction kinetic multiplied by that deactivation function for the main reaction. And, divide by same thing for here so main reaction kinetics for U formation times its deactivation function. And, that simply because now kD divide by kuCA to the power n minus m. So, it will depend on the order with respect to main and the poison reaction time the phi1 by phi2. So, this is again it may not be same phi1 and phi2. So, that is what the overall selectivity for deformation.

So, now D phi1 over dt which is your deactivation rate for first reaction that is deformation so kdD deactivation constant times it can be some activity power like phi1 to the power p and it may also depend on the concentration of the feed or may not. So, it depends on the concentration of feed it is more generalized. So, CA to the power some r same thing for decreasing activity for second reaction which is minus dA by d2 or d phi2 by dt either way one can write is equal to rdu and that is equal to kdu. That is deactivation constant for U formation times it is A that is activity of that second reaction toward second reaction to the power q and times the concentration of A to the power S. Again here we have assumed that it may depend on the concentration of the poison precursor present in the field which is related to the concentration of the main field. So, one can impregnate the expression and find out what how phi1 changes or activity for first reaction change and activity so this is one five one as usual d five one divide by five one to the power p so separation of variables.

So, impregnation of separation so one can find out the phi1 which is something like this so you can do it when you practice. So, just integrate this equation and phi1 is equal to 1minus p plus 1 times kdDCA to the power r times t to the power 1 over plus p minus. So, here it is just time and this is you know that it will be this minus p so p plus 1 minus p plus 1 divide by minus p plus 1 and that is what written here. Same thing for the second reaction so one can relate phi2 also and this can be substituted in the main reaction which is written here.

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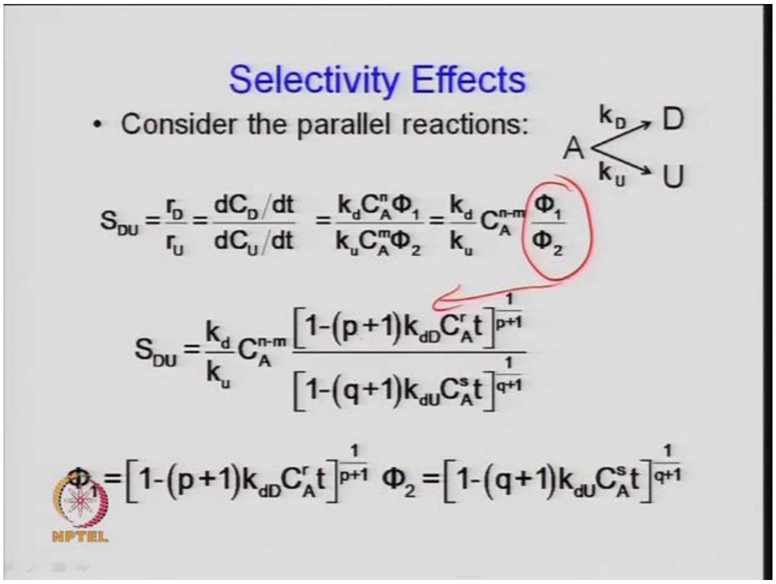

Selectivity Effects

- Consider the parallel reactions:

$$A \begin{cases} \xrightarrow{k_D} D \\ \xrightarrow{k_U} U \end{cases}$$

$$S_{DU} = \frac{r_D}{r_U} = \frac{dC_D/dt}{dC_U/dt} = \frac{k_d C_A^n \Phi_1}{k_u C_A^m \Phi_2} = \frac{k_d}{k_u} C_A^{n-m} \frac{\Phi_1}{\Phi_2}$$

$$S_{DU} = \frac{k_d}{k_u} C_A^{n-m} \frac{\left[1-(p+1)k_{dD}C_A^r t\right]^{\frac{1}{p+1}}}{\left[1-(q+1)k_{dU}C_A^s t\right]^{\frac{1}{q+1}}}$$

$$\Phi_1 = \left[1-(p+1)k_{dD}C_A^r t\right]^{\frac{1}{p+1}} \quad \Phi_2 = \left[1-(q+1)k_{dU}C_A^s t\right]^{\frac{1}{q+1}}$$

So, SDU is equal to rD upon rU which is written in terms of these two rates and can be recohilated with the kD times CA to the power n which I have already talked. And, that can be now substituted because this ratio is known now. So, this is just a substitution of this term here, So, how the selectivity change? Because, of the deactivation will depend on the orders of each that is the first one towards d and the second one towards q or U. And, also the concentration of the field if that depends and that will change with time on stream. So, one can write the selectivity expression for the product overall it will depend on n minus m also if that change. That is the order is different for main reaction that is formation of the D and formation of the U.

So, one can very easily find out that how selectivity changes with the reaction and can correlate with the activity of the catalyst. So, it means that the activity of a catalyst change or because of that the selectivity towards a particular product or desired product may also be affected. So, deactivation may have many consequences. So, one needs to understand the mechanism for catalyst deactivation for a given reaction and selecting a given catalyst. Because, it change from catalyst to catalyst also. So, all kind of deactivation need to be studied and then it should be in the main reaction and finally for the reactor desire. Because, the selection of catalyst or screening of catalyst will depend on the stability of the catalyst also which is the part of the catalyst deactivation.