Chemical Reaction Engineering II
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Lecture - 27
Fluid-solid non-catalytic reactions I

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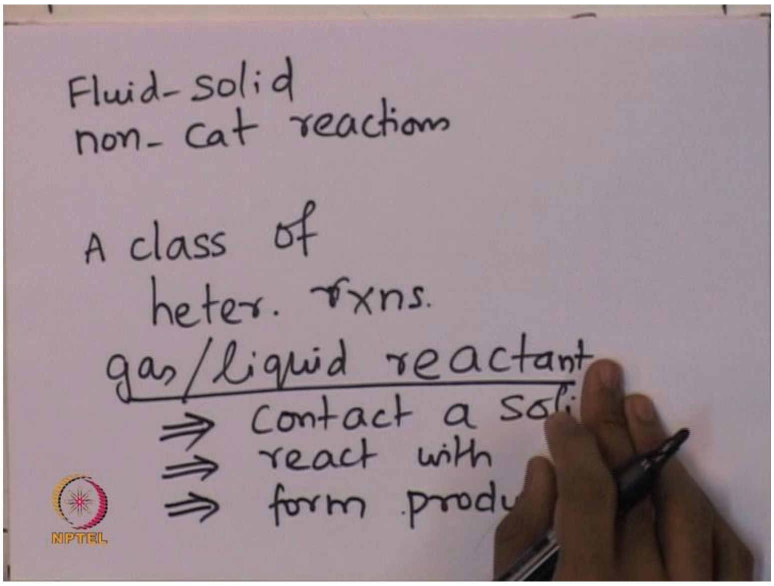

Fluid- solid
non- cat reactions

A class of
heter. rxns.
gas/liquid reactant
⇒ contact a sol
⇒ react with
⇒ form produ

Friends, let us look at fluid solid non catalytic systems. In the next 3 lectures we are going to look at what are the different aspects related to fluid solid reactions in non catalytic systems. And how to appreciate the reaction process which is occurring in the solid in non catalytic systems and how to model these systems? So, the fluid solid non catalytic reactions fluid solid non catalytic systems. So, these are essentially heterogeneous reactions which were the gas or the liquid they actually if come in contact with the solid and then they react with the solid and then they transform the reactants into our products.

So, these are a class of heterogeneous reactions these are a class of heterogeneous reactions where, the gas or a liquid which is essentially a reactant a gas or a liquid reactant they come in contact with the solid they contact a solid and then they react with the solid with solid and then form products. So, this is very common in many industrial settings and we are going to see several examples of these today and also to look at how to model these systems.

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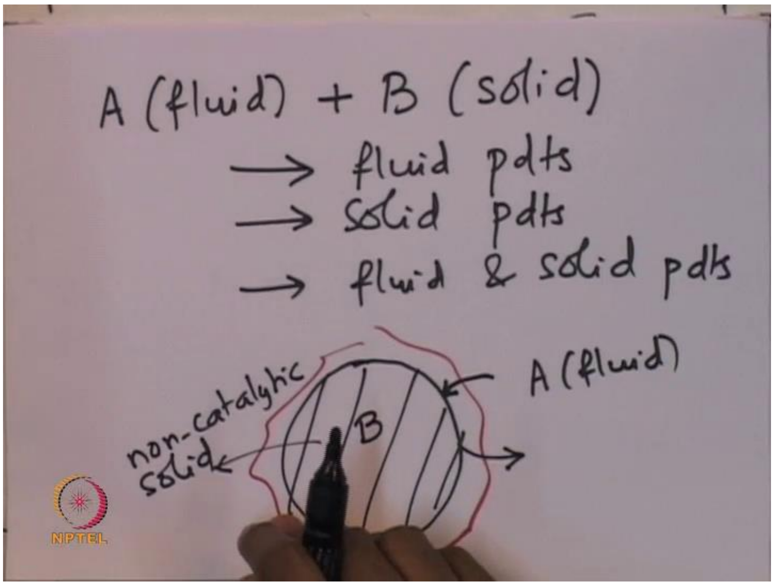

A (fluid) + B (solid)

→ fluid pdts

→ solid pdts

→ fluid & solid pdts

So, suppose if the reaction is in general if suppose there is a fluid A which is a fluid it may react with a solid b to form types of products. So, there are various possibilities 1 is the product might be a fluid; so it might be fluid product. So, the fluid reacts with a solid b and then it forms a fluid product or it might form a solid product might form a solid product or it might form a combination of fluid and solid products together.

So, any of these 3 the possibility any of these 3 can occur, because of a fluid solid non catalytic reaction. So, now if I look at what happens exactly suppose, if there is a catalytic core suppose if there is a solid and it is a non catalytic solid it is a non catalytic solid core which is present. Then suppose if this is B, B is that particular reactant and there might be A which is in the fluid stream which might be present around this particular solid might be present around the solid; might be percent around the solid.

There the species a now moves into the solid, and then it reacts with the particular species B, and then the product is now removed from this B from this particular species. Remember that it is a non catalytic system.

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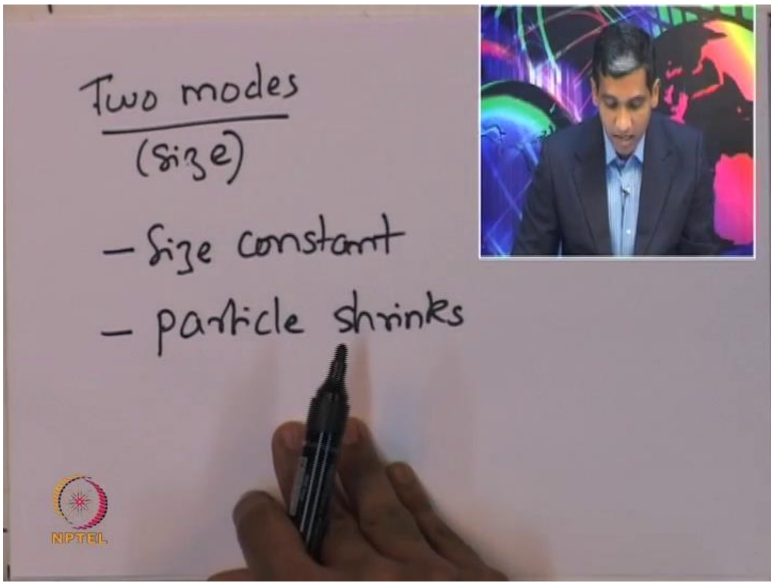

Two modes

(size)

- Size constant
- particle shrinks

So, now, there are 2 possibility there are 2 possibilities or 2 different classes of such type of fluid solid non catalytic systems. So, I could call I call it 2 modes there are 2 modes that are possible 2 particular modes.

This mode at this classification is based on the it is based on the size of the size of this solid core which is actually participating in the heterogeneous reaction. So, 1 more is where the size remains constant 1 mode is where the size of the solid core which actually remains constant. Another 1 where the size actually shrinks that is the particle actually shrinks. So, there is a change in the size of this solid particle.

So, there are 2 modes based on a classification based on sites 1 is the 1 is where the size remains constant, the other 1 is where the a size actually shrinks. Here, it is assumed that the density of the solid reactant and product are not very different. It should be noted that if the densities are different then the particle can also expand.

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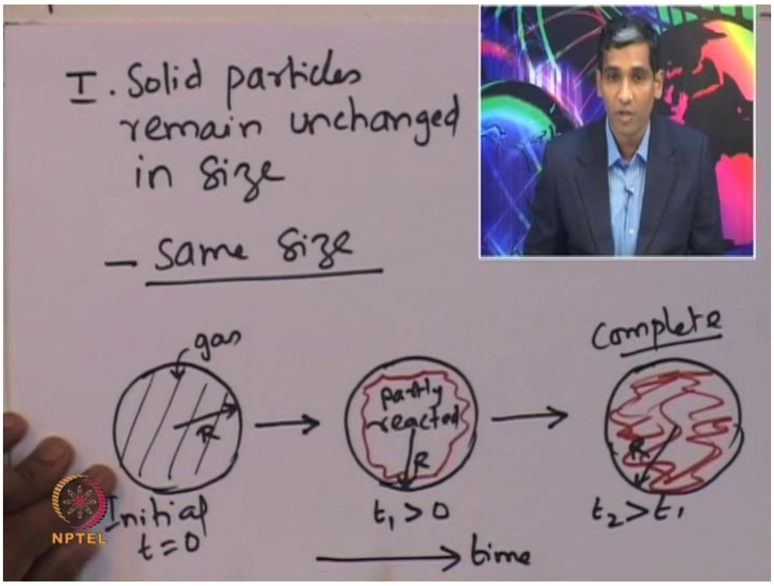

I. Solid particles remain unchanged in size

– same size

So, let us let us look a little bit more deeply into these 2 modes. So, the first mortars where the solid particles solid particles remain unchanged in size that is remain. So, the size remains same which means that it is a same size all through it is a same size all through the action is being conducted. So, now suppose if I have a solid suppose if I take a spherical particle, now this is the initial unreacted solid core. So, let us say at time y equal to 0.

Now, as the reaction proceeds suppose there is a gas which is present outside and the gas actually gets into the solid and there is a certain reaction which is happening. And after certain time what happens is let us say that there is in this particular case there is a that the size does not change. And so there is some parts some parts of the solid core which is actually undergone a reaction. So, there might be … So, it is basically partly reacted.

So, it is a partly reacted, remember that the size does not change. So, if the radius of this core is r the radius continues to remain ass approximately the same size as the initial size of the particle. So, this might be some time t 1 which is greater than 0 then as time further proceeds as the reaction proceeds to further conversion as there is more conversion of the reactants. Then 1 can see that suppose if this is the size or this is the particle where remember that the size remains same size does not change in this particular mode.

However, there is more amount of reactant which gets converted. So, this could be like a completely converted situation where t 2 which is greater than t 1. So, as time proceeds … So, this might be a complete conversion; this might be a complete conversion situation. So, as time proceeds slowly the gases will go inside and then the reaction will start occurring from the outer periphery and then it will start going into the reactants will go inside and the reaction will proceeds inside and the complete conversion will occur. Overall the reaction occurs the size of the particle does not change.

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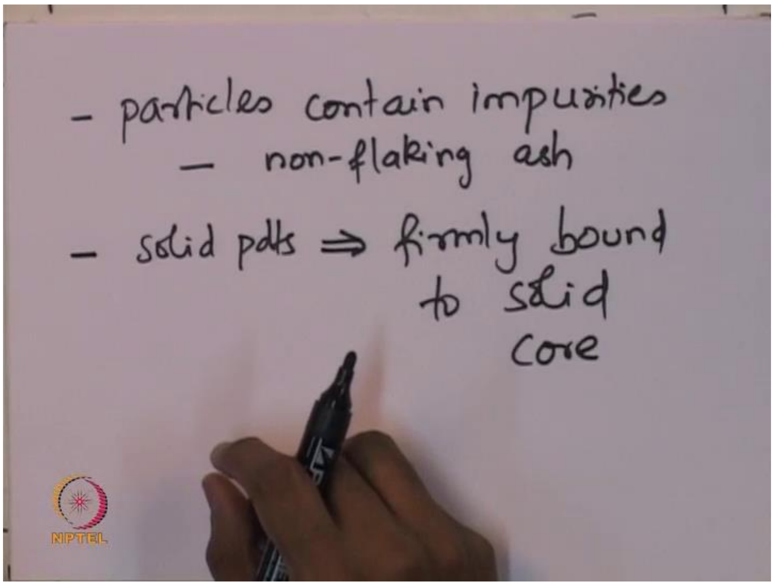

- particles contain impurities
  - non-flaking ash
- solid pdts ⇒ firmly bound to solid core

Now, how is this possible this particular mode is possible when the particles they contain lot of impurities. So, these impurities are actually they are tightly bound to the solid core. So, these impurities are tightly bound to the solid core and they remain as a non flaking ash.

So, what happens is these impurities after the reaction is actually being conducted. So, these impurities continue to stay inside the solid core and therefore, it preserves the shape and size of the solid core. And therefore, these impurities they remain as non flaking as the reaction proceeds. And the other possibility how this particular mode can actually occur is where the products are actually solid products.

If solid product are formed they are firmly bound to the solid core. So, if the solid products form and they are they are very firmly bound to the core in which the heterogeneous reaction is occurring then the size does not change it actually preserves the size and pretty much the shape of the solid. So, this particular this aspect actually helps the solid core to retain its shape.

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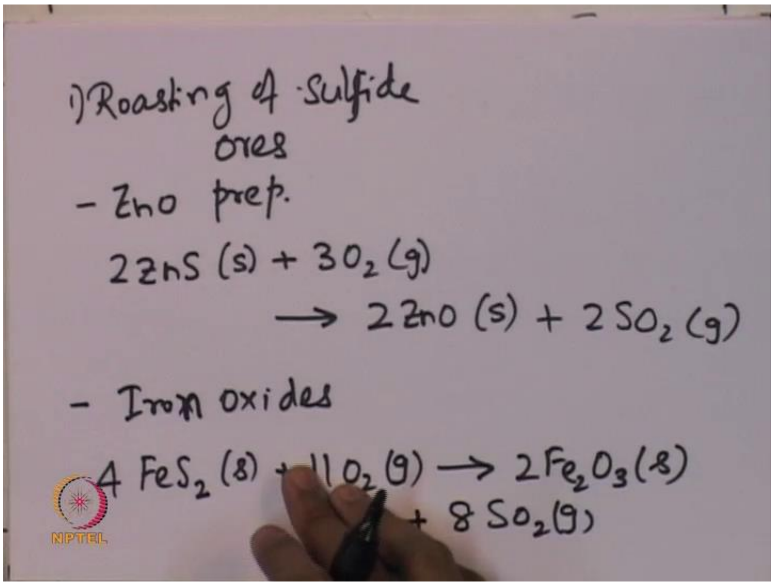

i) Roasting of Sulfide ores

- ZnO prep.

$2ZnS\,(s) + 3O_2\,(g) \longrightarrow 2ZnO\,(s) + 2SO_2\,(g)$

- Iron oxides

$4\,FeS_2\,(s) + 11O_2\,(g) \longrightarrow 2Fe_2O_3\,(s) + 8\,SO_2\,(g)$

So, now let us look at a few examples of few realistic example of where under what is what kind of systems this mode has been observed. So, the 1 good example is where the roasting of sulfide ores. So, toasting of sulfide ores is basically a sulfide form for example, a zinc sulfide and roasting process is where the there is an oxidation reaction. So, the oxygen is these zinc sulfide is exposed to oxygen under certain conditions and it lead to formation of the zinc oxides.

So, it is basically formation of zinc oxide from zinc sulfide and zinc oxide is a zinc sulfide is actually available methane in solid form and oxygen, which is a fluid, undergoes a non catalytic reaction and it leads to the formation of the zinc oxide which also is a solid product. So, therefore, the nice example is where it is a zinc oxide preparation and the reaction scheme is 2 zinc sulfide and 3 oxygen molecules. They combine together of form 2 zinc oxide which is again in the solid form and then it leaves out sulfur dioxide.

So, that is the reaction scheme. So, this particular example actually the reaction follows the first mode of a fluid solid non catalytic heterogeneous reaction type, where the size of the zinc sulfide particles sulfide ore that was used does not change much in the size. So, the actual industrial process is the ore is taken and it is crushed and then its sized into a certain size. And then it is put into a certain type of reactor where the oxygen the air is being fed and then it reacts with zinc sulfide and then forms the zinc oxide which is a solid product.

Another example of that is the preparation of iron oxides and the way it is done is 4 times 4 ferric sulfide in the solid form that reacts with eleven molecules of oxygen and that gives 2 Fe2O3 solid and 8 sulfur dioxide yes. So, that is another example of reaction its heterogeneous reaction which follows this first mode of fluid solid non catalytic reaction. Another example is where we have magnetite which is Fe3O4, which is actually being reduced for the formation of the metal ion.

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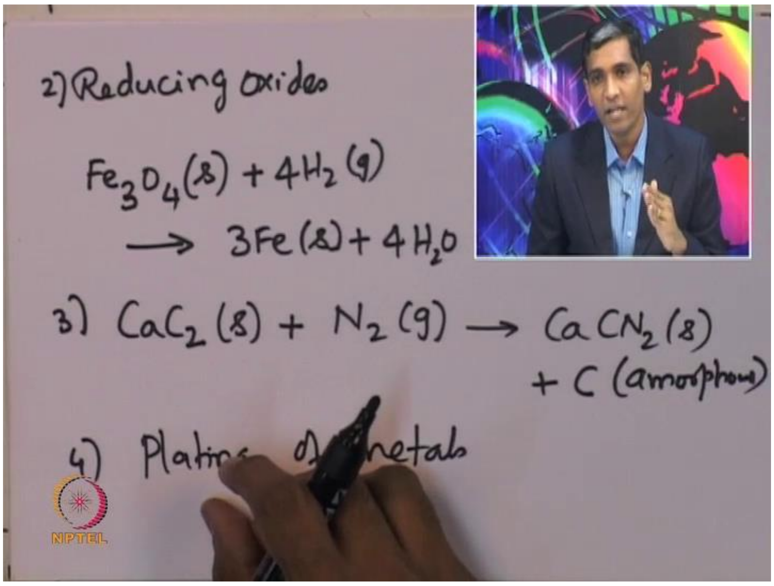

2) Reducing oxides

$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O$

3) $CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C$ (amorphous)

4) Platin[illegible] metals

So, the second example reducing oxides; so in the case of reducing oxides what happens is that the Fe3O4 which is actually press as in the solid form as a natural ore. Is actually it is it is called the magnetite what is done is it is actually crushed and then it is sized and then it is actually fed into a counter current fluidized bed reactor continuous counter current fluidized bed reactor, the presence of hydrogen. And this particular a presence hydrogen it gets reduced to forming the iron metal iron.

So, the action scheme is plus 4H2 which is again in the gas form that leads to the formation of 3 times Fe plus 4 times H20. So, that is the reaction scheme which is used for reducing the oxides. Another example is the is the formation of calcium cyanamide where CaC2 which is basically the calcium carbide that is that is which is again for present in the a solid form and that reacts with the nitrogen N2. And that leads to the formation of CaCN2 which is again a in the solid form.

Then it also leaves a amorphous carbon as deposits amorphous carbon as deposits. So, clearly in these examples that is a there is a solid product which is formed which gets deposited onto the solid core in which the fluid solid non catalytic reaction actually occurs and this helps in preserving the size of the core. Another example is basically the plating of various metals all metals. So, far various purposes different metals are actually coated onto the surface using this method called electroplating.

So, in this plating where the original core does not change, but then the, but then the reaction actually occurs in fluid solid non catalytic reaction actually occurs without changing the size of the original solid core.

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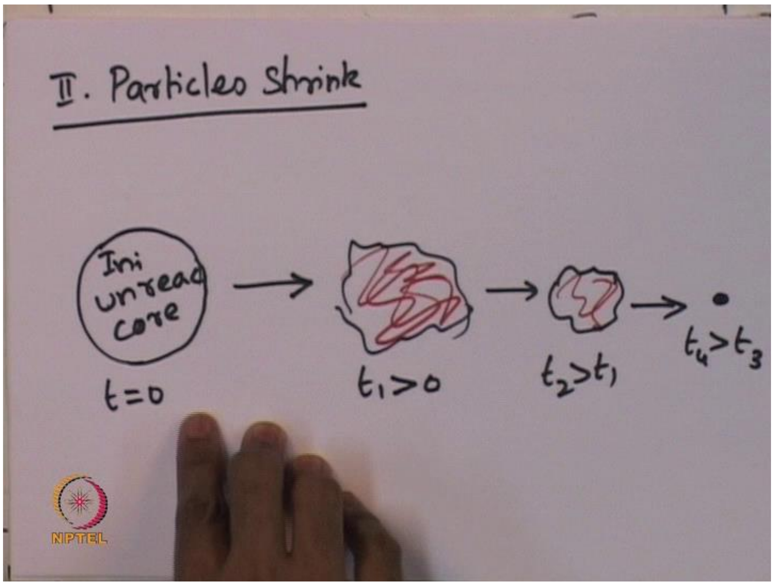

So, the second mode is basically where the essentially the particles shrink. So, there is a shrinking of the particles. And in this particular case what happens is suppose if this is the initial unreacted core; so let us say at time t equal to 0.

So, as time proceeds the size of the particle changes because the solid is now being used and then it is converted into products and then it is being consumed. So, there is a reduction in the size of the catalyst particle and that is at let us say time t1 greater than 0. And there is still unreacted core which is present inside this is the unreacted core which is reduced in size and then as time further proceeds the size further reduces down. So, this is let us say t2 greater than t1, that is the further time and then ass time proceeds further it gets reduced into the solid core actually disappears.

So, this is because the solid this solid which is percent in the initial unreacted core is now almost completely consumed. So, as time proceeds we can see that the core is slowly being consumed and then the core completely disappears. The particle can deduce in size even when there is a product layer around it. So, there are several examples where that this particular mode of heterogeneous reaction occurs.

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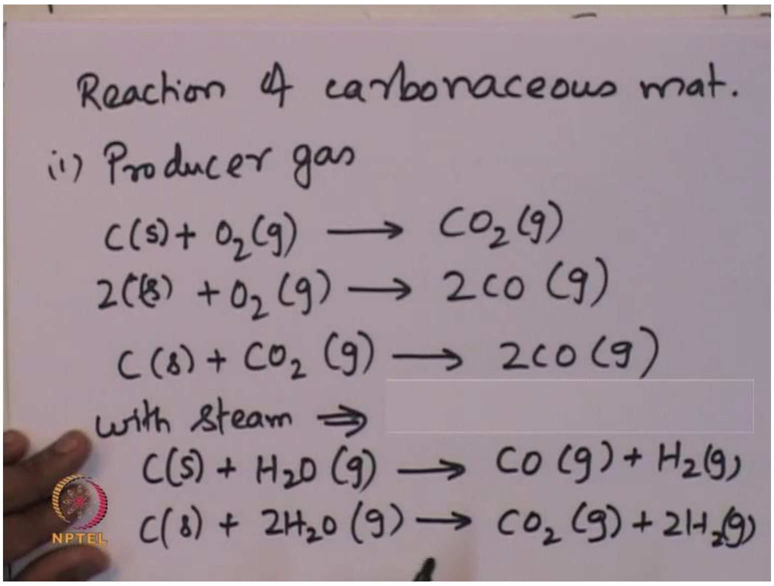

Reaction of carbonaceous mat.

(i) Producer gas

$C(s) + O_2(g) \longrightarrow CO_2(g)$

$2C(s) + O_2(g) \longrightarrow 2CO(g)$

$C(s) + CO_2(g) \longrightarrow 2CO(g)$

with steam ⇒

$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

$C(s) + 2H_2O(g) \longrightarrow CO_2(g) + 2H_2(g)$

Typically this occurs when there is reaction that involves of carbonaceous materials. So, typically reactions that involve carbonaceous material they generally follow this mode where the size of the solid core actually constantly decreases and then the core eventually disappears. So, a nice example of that is the production of the producer gas and this is generally performed at a the air limiting conditions and. So, the reaction scheme is that carbon which is present in the solid form that reacts with oxygen which is in the gaseous from and that leads to the formation of Co2 in the gas form.

Now, similarly another scheme which occur simultaneously is a carbon it reacts with oxygen to form carbon monoxide this again occur simultaneously along with the first reaction and then another reaction which also occurs with is carbon when it reacts with

Co2. So, Co2 which is also formed by this reaction it again interacts with the unreacted carbon which is present in the solid core and that leads to formation of 2 Co2.

So, this is the reaction scheme for producer gas suppose if the reaction is conducted within the presence of steam then it leads to the formation of Co Co2 and H2 which is the carbon gasification reaction and this scheme is carbon and water at. So, steam is essentially the vapor form of water and that leads to Co and H2 and carbon in the presence of 2 water molecules that lead to formation of Co2 in the gas stream and 2 hydrogen molecules.

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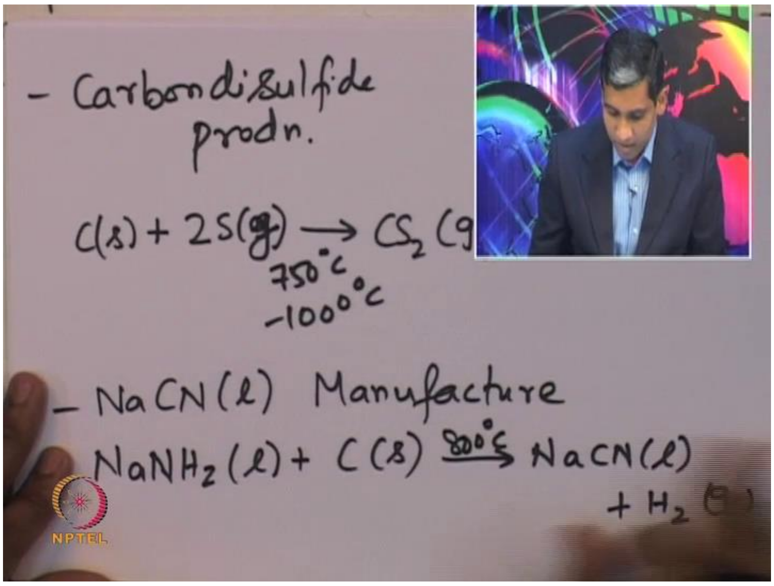

- Carbondisulfide prodn.

$$C(s) + 2S(g) \xrightarrow[750^\circ C - 1000^\circ C]{} CS_2 (g$$

- NaCN(l) Manufacture

$$NaNH_2(l) + C(s) \xrightarrow{800^\circ C} NaCN(l) + H_2 (g)$$

So, both these reactions typically occur in a situation where the solid core which is basically unreacted carbon when you start to start with it is truly being consumed and then the carbon eventually disappears. So, that is basically the mechanism that is been observed for in the producer gas production. So, similar process actually occurs in the manufacture of carbon disulfide suppose if we look at carbon disulfide production.

If you look at carbon disulfide production then the reaction scheme is carbon in its solid form reacts with 2 sulphur molecules which is again in the in the gas form and that leads to the formation of c s 2 and this typically occurs at 750 degree to 1000 degree c. So, that is and at a very high temperature. So, carbon in this solid form which is again percent as an as a core solid core and sulphur which is the gas stream reacts to form the sulphur carbon disulfide.

Another example is the manufacturer of a sodium cyanide. So, manufacture of sodium cyanide sodium cyanide manufacture and the reaction scheme is sodium n a n H2 in the liquid form it reacts with the a solid carbon solid core and that leads to the formation of NaN aCN in liquid and it liberates hydrogen. So, that is the reaction scheme and it is typically conducted at 800 c.

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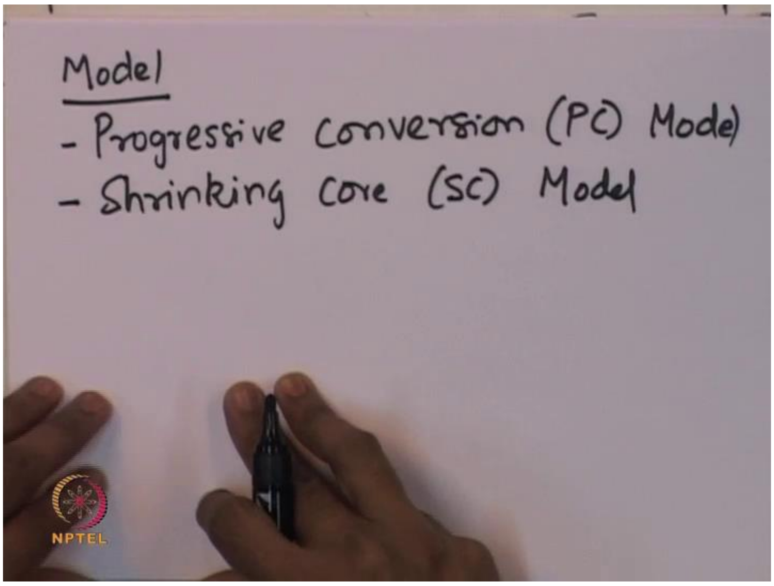

Model

- Progressive conversion (PC) Model
- Shrinking core (SC) Model

So, that is another example where the core actually shrinks and eventually disappears. So, there are many other processes for which such kind of a such mode of fluid solid non catalytic reaction have been observed. So, now … So, let us attempt to model this system model the fluid solid heterogeneous reaction. So, there are 2 types of models that have been proposed. So, the first model is called the progressive conversion model I call it PC model.

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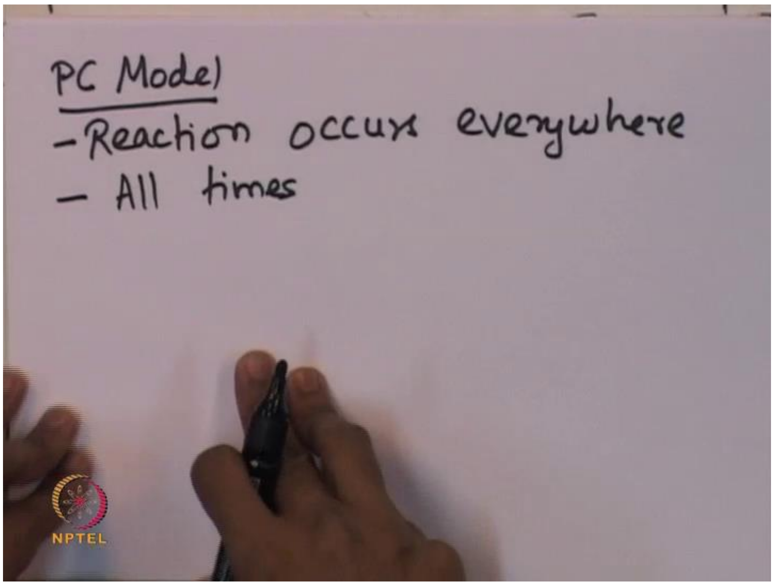

PC Model

- Reaction occurs everywhere
- All times

So, the first model is called the progressive conversion model and the second model is called the shrinking core model. So, the shrinking core model is much more well known and more applicable to many systems than the progressive conversion model; however, let us look at let us look into the details of what these 2 types of models are which to represent the fluid solid non catalytic heterogeneous reactions. So, let us start with PC model the progressive conversion model.

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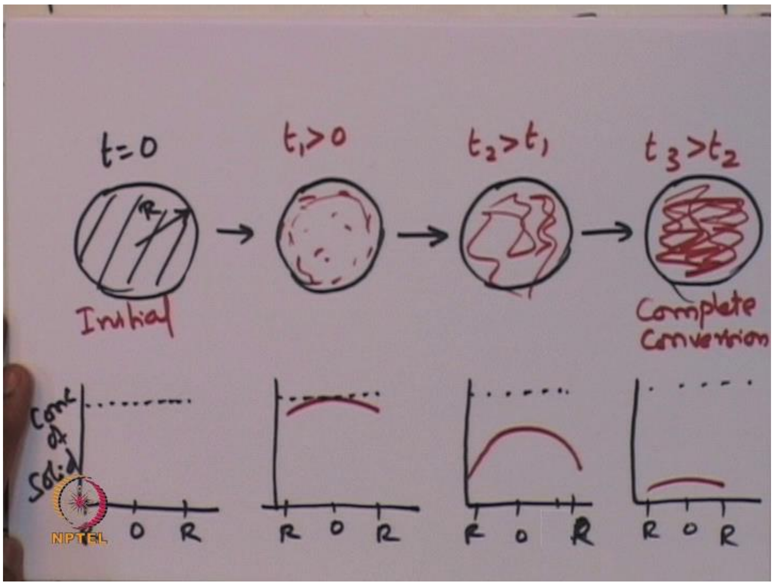

So, progressive conversion model assumes that the reaction occurs everywhere reaction occurs everywhere and not just that it occurs everywhere it occurs everywhere at all times. So, it assumes all the time till complete conversion the action occurs everywhere in the solid core. So, suppose if I if we attempt to capture this assumption what it suggests is that suppose if there is an initial core suppose if this is the initial core that is at time t equal to 0.

So, that is the initial core which is filled with the solid reactant now as time proceeds reaction occurs in the in the solid core everywhere. And let us say at time t 1 which is greater than 0 and then at a further later time what happens is that the reaction occurs further. And suppose if this is the solid core reaction occurs further and more reactant is being consumed more solid as being consumed again the action is actually occurring everywhere inside the reactor.

However, the rate of reaction that is occurring in different locations could in principle be different. So, this might at t2 which is greater than t1 and then at a further later time most of the reactors which are actually present in the solid core have actually being reacted. So, suppose if the intensity of the red color here suggests the extent of reaction at different times then at t3 which is greater than t2 1 may assume that the complete conversion has been occurred.

So, this might be the initials initially when the solid is actually percent everywhere in the core and this is basically when the complete conversion has occurred now suppose if we if we attempt to sketch the concentration profile in each of these time steps. So, we can says sketch in the following way suppose if the radius of the particle is r and between 0 and r the concentration of the solid initially it reminds it let us assume that it is uniforms.

So, this is the concentration of solid let us assume that it is uniform and then as time progresses at a later time let say this is the initial concentration, but because the reaction is occurring uniformly reaction is occurring all though the particle it may be non uniform because it the rates may be different in different locations. So, we can sketch the profile in this way. So, the concentration of the solids will at time t which is greater than 0 this is the kind of profile.

Now, at a later time at a later time what happens is that because in the action is occurring everywhere inside the solid. So, the concentration of the solid would actually decrease at every location inside the inside the solid core. So, therefore, the kind of profile that 1 would expect is something like this where this is the end of this is basically R and at a much later time when the conversion is expected to be complete. And so if this is the initial a initial solid concentration and this is R.

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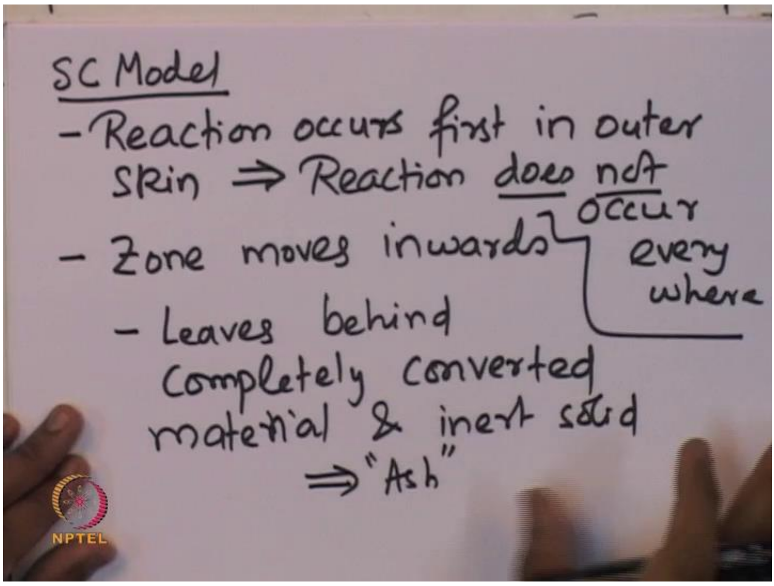
SC Model

- Reaction occurs first in outer skin ⇒ Reaction does not occur every where
- Zone moves inwards
  - Leaves behind completely converted material & inert solid ⇒ "Ash"

.

Then the concentration of the a solid inside the inside the solid core will be almost 0. So, clearly you can see that there is a progressive decrease in the concentration of the solid all through the solid core. So, this is an important assumption that is actually made by the progressive conversion model. So, next let us look at the a shrinking core model. So, the shrinking core model assumes that the reaction first occurs in the outer skin reaction occurs in outer skin.

Then assume that the reaction zone actually moves inwards. So, the first assumption also means that the reaction does not occur everywhere the first assumption also means that the reaction does not occur everywhere in the solid core. Unlike what was assumed in the progressive conversion model and it also because of this proper. This because the reaction first occurs in the outer skin these reactions zone actually starts moving inward as the reaction proceeds.

Then once it moves into as the reaction zone moves inside what it does is it leaves the leaves behind completely converted material. So, it leaves behind the completely converted material and also some of the inert solids which may already be present in the solid core. So, the converted products are now assume that it sticks back into the a solid core and whatever inert solid which is unreacted they also will stick back in this solid core.

So, these 2 together is clubbed as ash. So, the ash to the ash in the in the solid core is basically a combination of the products which are actually completely converted material and also the inert solids which would have not reacted in the action. So, these 2 are called as ash products know if we attempted to depict the concentration profiles. If we attempt to intuit what is the concentration profile, in the solid core in if you assume a shrinking core model is essentially it looks like this.

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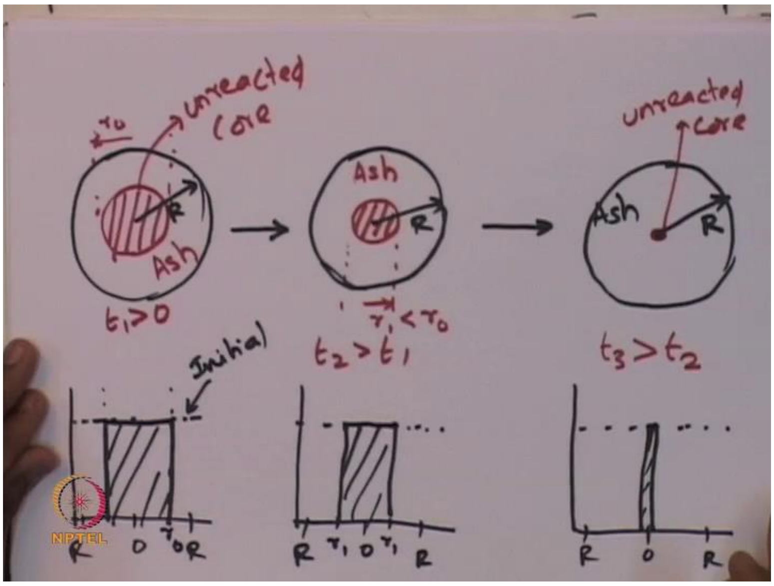

Suppose, if this is the solid core and let us say at some time as the reaction has started at some time if this is the unreacted core remember that the shrinking core model assumes that the reaction first occurs at the outer skin and then the reaction front starts moving towards the inwards of the solid core. So, which means that at any time there’ll always be an small unreacted core until the conversion is complete.

Which means, that all the solid has been consumed. So, till all the solids have been consumed there’ll always be some location where the unreacted solids are present. So, let us sat at sometime t 1 which is greater than 0. So, this is the same amount of unreacted core which is percent and the outside layer is called the ash layer now as time proceeds as time proceeds. Then the scenario will be if this is the solid core which was started initially and the reaction as start this is the initial size of the solid core r is the initial size of the solid core.

So, now the unreacted core will start shrinking in size because the reaction fronts have started moving towards the center of the solid particle and there will be again ash which is percent outside this so the radius of this unreacted core, if I call this r1. So, this r1 will be smaller than the radius of the unreacted core which was present at an earlier time. So, this is r naught small r naught.

So, if that radius will be smaller than this r naught which means that the reaction front has moved inside and the solid which is present between r naught and r1 has now reacted to form products. So, this is at let us say time t 2 which is greater than t 1 and at a later time. So, if this is the original size of the solid core which is to be which in which the reaction was started then the unreacted core will now reduced to a very small size until it completely disappears.

So, this is the unreacted core and everything outside is basically ash now where it is pretty much converted and this might be at a at a later time t3 which is greater than t2. So, now if we look at the concentration profile for this situation if this is 0. So, at this time the solids are present only in this unreacted core. So, therefore, the concentration of the solids will essentially be the concentration all of the solids which was present initially everywhere.

However, it is present only so this is the initial concentration. So, this is the initial concentration of the solids then at this particular time t 1 the solids are present only in this location between 0 and r naught. However, the concentration will be as much as the initial concentration itself and then at the next time step. So, the region where the … So, unreacted solids are present is now going to shrink; however, the concentration in that location will continue to remain as that of the initial concentration.

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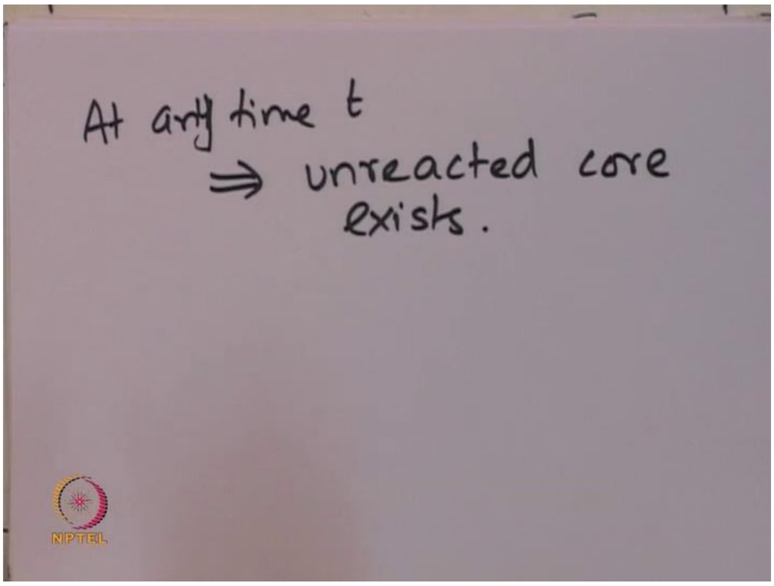

At any time t

$\Rightarrow$ unreacted core exists.

Then if I once again plot at a much later time this particular this region will start shrinking. So, this is a 0 so 0 is the center of the sphere and. So, the unreacted solid are now present only in the in this very small region which is around the center of this particular sphere. If we assume that the solid core in which the reaction is started is actually a a spherical particle. So, what this model assumes that at any time there always exists at anytime unreacted core always exists.

So, this might be very small or very big, but the at time there's always unreacted core that exists. So, now, there have being experiments that have been performed where the catalyst particle where the solid core after the reaction has occurred which is again a non catalytic reaction has actually been broke has been cut opened to check the extent of carbon that has been consumed. So, if it is a carbonaceous the action after some certain conversion, at different times if the carbon can actually be cut open and then looked at what is the extent of consumption of carbonaceous material towards forming the corresponding product.

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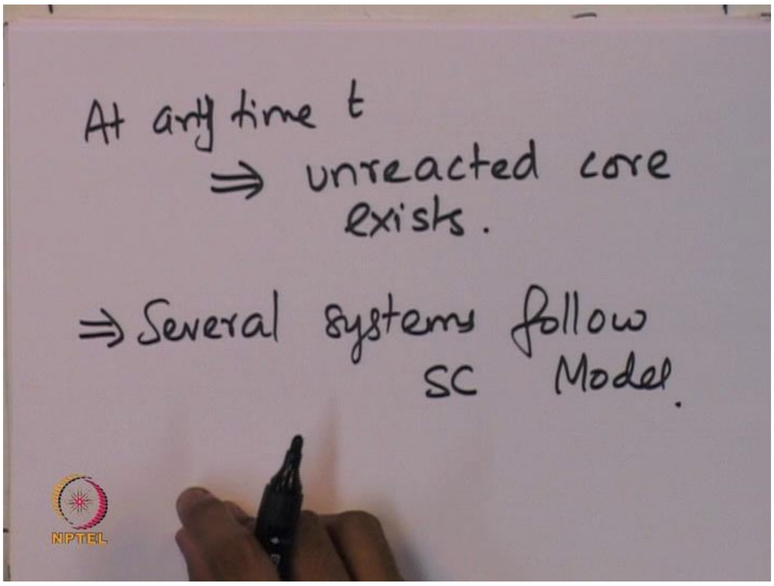

At any time t

⇒ unreacted core exists.

⇒ Several systems follow SC Model.

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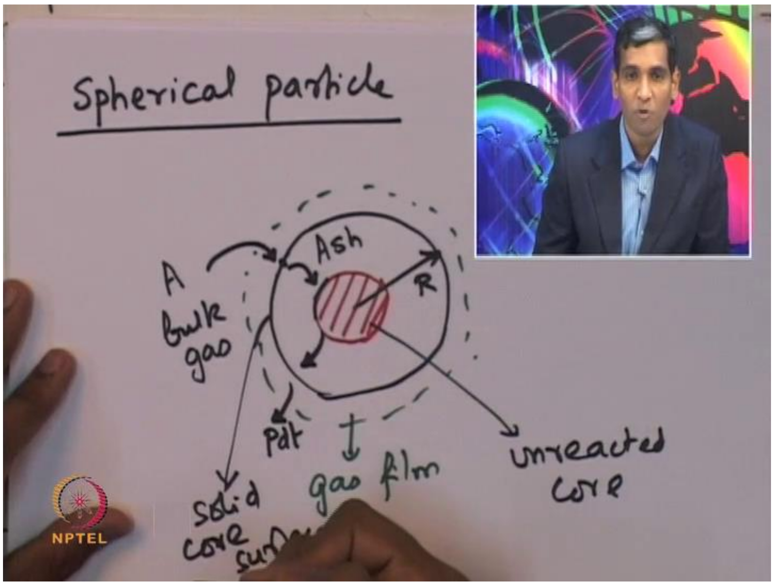

Spherical particle

So, it has been observed that for that several systems actually follow this shrinking core model. So, now … So, let us look a little bit more deep into what exactly happens in the shrinking core model because it is actually very relevant that many systems actually follow a shrinking core model. Suppose, if we assume that it is a spherical particle suppose if we assume spherical particle then if this is the initial core.

So, let us say that there is a spherical particle and of radius r. So, that is the initial core that was actually started with and let us assume that the unreacted core is actually present somewhere here. So, that is that is again concentric with the let us assume that it is concentric with the periphery of these spherical particle and then if we assume that there is a there is the gas which is present outside then there will be a small gas film.

So, this gas film will exist around this spherical particle and the gas which is present in the bulk. So, let us say this is bulk gas stream this is bulk and this is the ash layer and this is the unreacted core. So, if species a let us see if this is the species a is present in the gas stream. So, the species a now first has to go into the gas film and then it has to go into the surface of solid core. So, this is the solid core surface. So, a has to now defuse into the surface of this solid core and then it has to defuse through the ash layer and it has to reach the unreacted court.

So, it has to reach the un location of the unreacted core remember that in this ash region there is no solid reactant which is present and therefore, no reaction is happening in the ash layer. So, the action actually happens only in the periphery of this unreacted core the moment the reaction occurs the the product which is formed has now has to diffuse through the ash layer and then it has to defused from the ash layer into the gas stream gas film and then to the bulk gas or let us say that this is the product.

So, the diffusion of the product … So, once the bulk species diffuses through the ash and then it reaches the surface of the unreacted core the product is formed and then the diffusion occurs and then the product leaves the spherical particle. So, this is the scheme that actually occurs in the this is how the this is the process that describes the describes the transfer of reactants into the solid core. And then the occurrence of the reaction in the unreacted core and the transport of the products back into the gas stream in the shrinking core type model.

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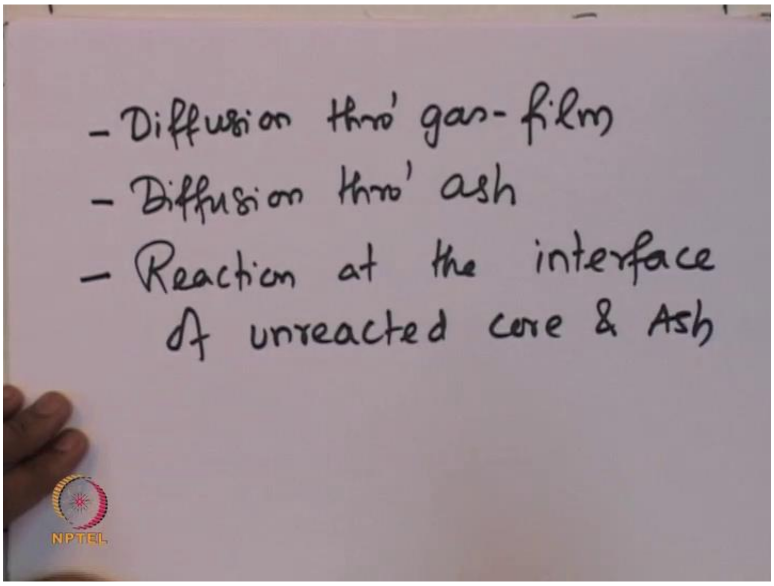

- Diffusion thro' gas-film
- Diffusion thro' ash
- Reaction at the interface of unreacted core & Ash

So, clearly there are 3 process which are actually occurring. So, the first process is diffusion through gas film and then the second process is diffusion though ash and the third process is reaction at the interface of unreacted core and ash. So, therefore, the extent of reaction that is the overall conversion all the of the of that reactant of the solid depends upon which of these 3 process is a rate limiting step.

So, it could be that the diffusion through the gas film is an extremely slow step. So, remember that the rate limiting step is essentially the 1 which is the slowest step. And because it is the slowest step it controls the actual reaction which is occurring in it controls the overall conversion. So, suppose the diffusion of the gas from the bulk to the surface of the core through the gas film if that is an extremely slow process. When can it be slow? If the effective diffusivity of the species through the gas stream to reach the surface of the solid core if that does that is extremely small.

If the if the diffusivity is very low then that can in principle serve as a as a rate controlling step now particularly when the reaction is faster that the diffusion step now the second possibility is where the diffusion through the ash. So, there is unreacted core and there is ash which is surrounding the unreacted core. So, the reactants have to now diffuse from the surface of the core through the ash and it has to reach the location where the unreacted core is present.

So, let me repeat the reactants have to actually diffuse from the periphery of the solid particle through the ash and it has to reach the surface of the unreacted core. So, if that diffusion of this reactant species through the ash layer if that is that is very slow then that an in principle be a limiting step. Now, the third possibility is where the reaction which is occurring at the periphery of the unreacted core. So, it that is an extremely slow if the net if the specific reaction constant is small then it can in principle actually be controlling and all the other processes can actually be faster.

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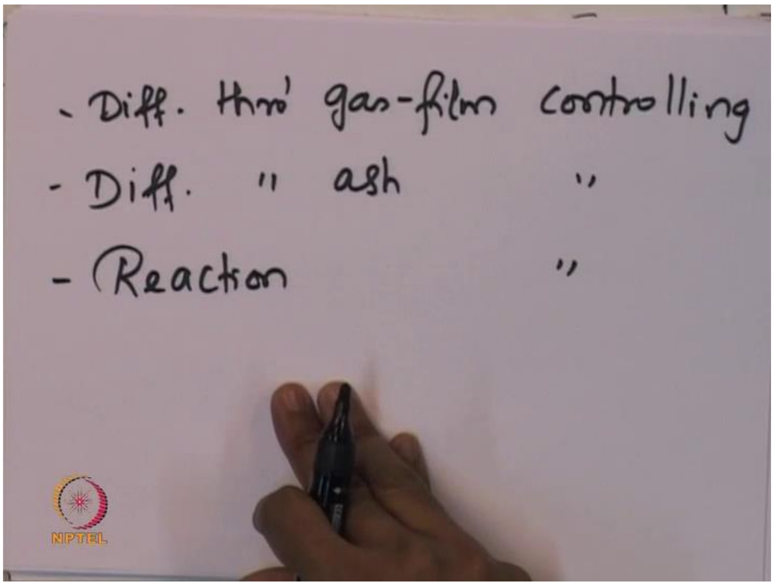

- Diff. thro' gas-film controlling
- Diff. " ash "
- Reaction "

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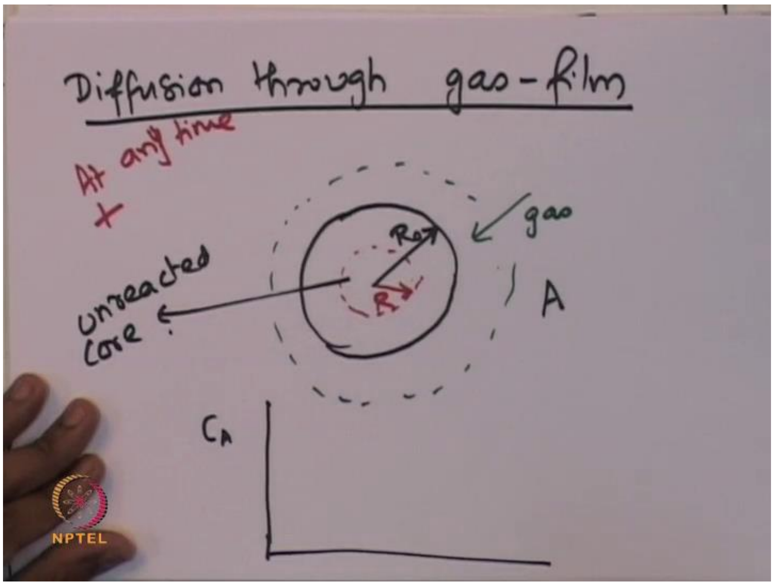

So, essentially there are 3 3 possibilities where. So, it could be diffusion controlling diffusion through ash layer controlling or reaction controlling. So, let us try to model each if model the system if the rate 8 controlling step any of these 3. So, let us start with the first 1 where we assume that the diffusion through gas film is the controlling step let us assume that diffusion through gas film is rate controlling.

Now, what happens here suppose if this is the this is the original particle with which the reaction was initiated and if the radius of this particle is let us say r and if the unreacted core is let us say act. So, let us say that the initial releases are not and the unreacted core is let us say at. So, let us say that the initial radius is r naught and the unreacted core the radius of the unreacted core it is depicted in red color here if that is r.

So, that is the at any time t at anytime t. So, the radius of the unreacted core is now r and the original radius of the particle with in which the reaction was initiated with r naught. And let us assume that there is a gas phase which is actually present around it. So, this is the gas phase and this is the unreacted core, now if we attempt to intuit what is going to be the concentration profile of let us say species which is in the gaseous form. And it now defuses through to actually react with the solid in the in this particle.

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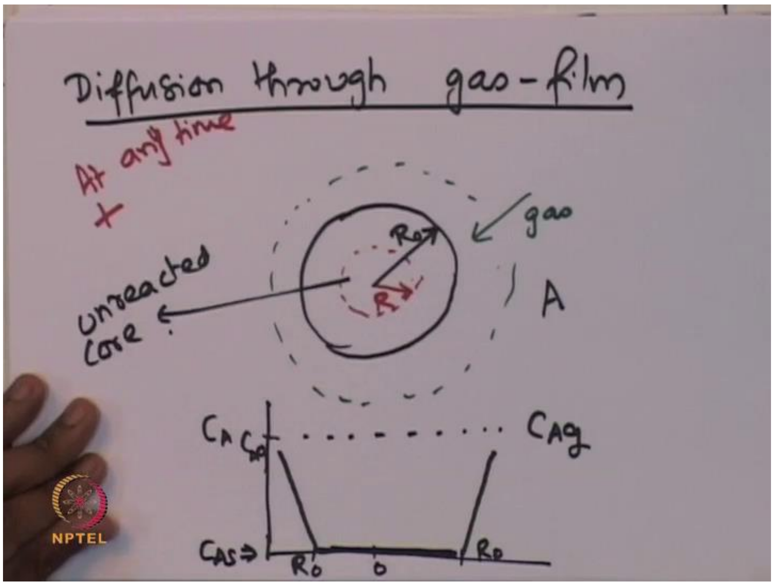

So, let is now try to intuit what is going to be the concentration of the species. So, suppose if this is the concentration of species a then because we assume that diffusion through the gas film is controlling the diffusion process in the gas film is going to be much slower than the other 2 processes which is actually occurring inside the solid core. So, therefore, we expect that there will be a concentration supportive if this is the bulk concentration c a g is the bulk concentration is the bulk concentration of species a.

Then if this we can expect that there'll be a concentration gradient in the gas film. So, this is at the center of the that is the centre of the core and this r naught that r naught and again this is r naught. So, we can expect that there will be concentration gradient outside the core and there’ll be no concentration gradient inside the core. And this is because as soon as the gas species actually enters the core that the reaction the reactant a will be immediately consumed. Because, it is a very fast process compared to the diffusion rate of diffusion of species a to the surface of the catalyst.

So, the concentration of the species inside the court is expected to be 0. So, that is the concentration inside the of the surface and also the concentration of the species inside the core. So, now, if we know this then how do we attempt to characterize this. So, we need to. So, if we need to if we need to understand the dynamics of the concentration change for this system we need to we need to start with a mole balance.

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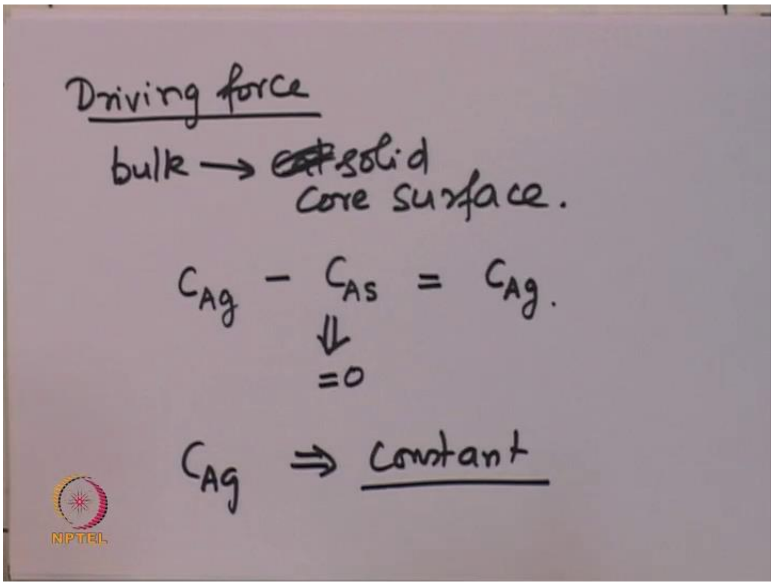

Driving force

bulk → ~~cat~~ solid core surface.

$C_{Ag} - C_{AS} = C_{Ag}$.

$C_{AS} \Downarrow = 0$

$C_{Ag} \Rightarrow$ Constant

So, suppose if the if the diffusion through the gas film is basically the a limiting step then the driving force the driving force for the species to get transported from the bulk to catalyst surface. It is the core surface of the solid core not catalyst that will be essentially be CAG which is the concentration of the gas concentration of the species in the bulk gas minus the concentration of the species in the surface.

But we know that because the reaction and the diffusion through the ash layer is faster compared to the diffusion of the species through the gas phase CAS is actually expected to be 0. So, therefore, the driving force is essentially the concentration of the species in gas phase itself. Now, suppose if we assume that the gas phase bulk concentration is constant suppose if we assume that this is constant which is reasonable. Because, in a real system we may be able to feed the gas at a certain rate in order to maintain a constant concentration of that particular species in the gas phase.

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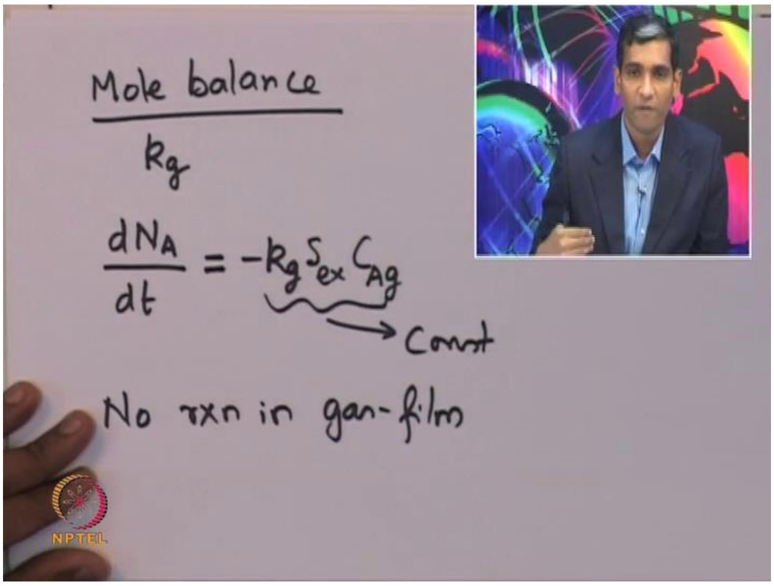

Mole balance

k_g

$$\frac{dN_A}{dt} = -\underbrace{k_g S_{ex} C_{Ag}}_{\rightarrow \text{Const}}$$

No rxn in gas-film

So, with this we can actually write a simple mole balance now the rate at which rate of change of the number of moles of species a with respect to time. That should be equal to the rate at which the species is coming in minus what at which the rate at which the moles are going out plus whatever is being generated. Now, the only process which is actually occurring here is basically the transport of the species from the bulk onto the surface of the core.

So, that that is actually a mass transport process. So, suppose if we define a mass transport coefficient k g then we can ride the rate as dNA. So, remember that a is the gas species which is actually moving from the bulk t to the solid core whether reaction is [uppering/occurring]. So, dNA by dt where n a is the number of moles of a which is actually diffusing from the bulk into the surface. So, the surface of the core and the reaction is occurring only inside the core and. So, there is no reaction in the gas phase.

So, there is no reaction in gas film. So, the only process which actually controls the rate of change of number of moles in the gas phase is essentially the transport of species from the bulk to the surface of the solid core because of diffusion. So, that should be equal to minus kg let us say that is the mass transport coefficient and typically the units are centimeters per second. And if s external is the surface area of the core external surface area of the core and that multiplied by the concentration of the species in the bulk phase.

So, that is the mole balance which captures the rate of change of a number of moles of species a in the gas phase. Now, because CAG is constant we can assume that this whole expression is basically a constant the S e x is basically essentially the external surface area of the core. And that is expected to be constant because we assume that the particle size is not changing significantly. And then kt is the mass transport coefficient there are several correlations which are actually available in order to estimate what is the mass transport coefficient for transport of a particular species from a bulk phase to the surface of a solid core.

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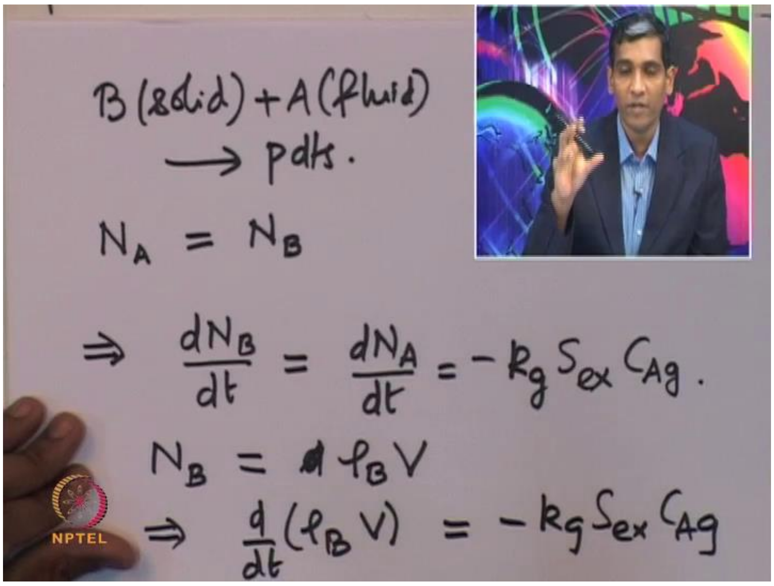

$$B\,(\text{solid}) + A\,(\text{fluid}) \longrightarrow \text{pdts.}$$

$$N_A = N_B$$

$$\Rightarrow \frac{dN_B}{dt} = \frac{dN_A}{dt} = -k_g S_{ex} C_{Ag} .$$

$$N_B = \rho_B V$$

$$\Rightarrow \frac{d}{dt}(\rho_B V) = -k_g S_{ex} C_{Ag}$$

CAG essentially can be maintained constant. So, therefore, the right hand side of this balance is essentially a constant. So, suppose we assume that b is solid which reacts with fluid a to form products then the we can assume that there is an equimolar consumption.

Suppose, if we assume that the b and a are basically under equimolar condition the reaction is occurring under equimolar conditions. Then the number of moles of which is consumed because of the reaction should be equal to the number of moles of b which is consumed because of the reaction.

Note that NA equal to NB is actually a special case and in general these 2 need not necessarily be equal. Now, why do we need this because we need to now monitor either then we can now monitor actually the amount of solid that is actually being consumed because of the reaction. And that is what is of interest and this the mole balance that was written for the gas species in the gas film can actually be used in order to estimate what is the number of moles of the solid reactant that was actually being consumed because of the reaction.

This is in the case of this no when the diffusion in the gas film is actually controlling the overall reaction. So, therefore, if n a is equally to n NB which is the number of moles of the solid that is being consumed in the action. And from here we can rewrite the mole balance as dNB by dt equal to dNB by dt and that is equal to minus k g which is the mass me made defeat transport coefficient into the external surface area multiplied by the concentration of the species a in the gas phase.

Now, we know that we know that the number of moles on the solid which is actually present in the in the solid is essentially given by the density of the species rho B multiplied by the volume and. So, we can rewrite this as d by dt rho B into volume that should be equal to. So, the number of a moles of solid which is present in the core can actually be related to the volume of the core by using this expression NB equal to density of the solid which is present in the core multiplied by the volume of the core at any instant time g.

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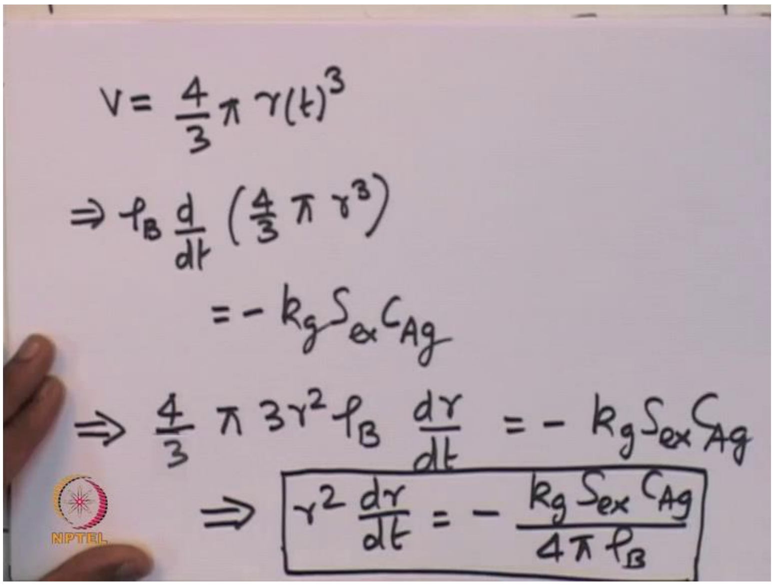

$$V = \frac{4}{3}\pi r(t)^3$$

$$\Rightarrow \rho_B \frac{d}{dt}\left(\frac{4}{3}\pi r^3\right)$$

$$= -k_g S_{ex} C_{Ag}$$

$$\Rightarrow \frac{4}{3}\pi\, 3r^2 \rho_B \frac{dr}{dt} = -k_g S_{ex} C_{Ag}$$

$$\Rightarrow \boxed{r^2 \frac{dr}{dt} = -\frac{k_g S_{ex} C_{Ag}}{4\pi \rho_B}}$$

So, remember that the volume changes as a function of time because as the reaction occurs the core is now shrinking and. So, the volume of the unreacted or volume of the unreacted solid core changes with time. So, if volume of because you assume that it is a spherical particle the volume is given by 4 by 3 pi r cube. So, remember that this r is a function of time because as time progresses the core actually shrinks in size and. So, the radius of the unreacted material is actually a function of time.

So, now if you plug in this expression in the mole balance you’ll find that rho b d by d t 4 by 3 pi r. Cube r is a function of time that should be equal to minus k g which is the mass transport coefficient into the surface area of the external surface area of the of the initial particles spherical particle, that was chosen multiplied by the bulk concentration of this reactant species a and. So, that can simply be rewritten as 4 by 3 pi 3 r square rho b and d r by d t CAG.

That will be equal to r square d r by dt that is equal to minus k g into CAG divided by 4 pi into rho b. So, that is the balance. So, that describes how the radius of the unreacted core actually changes with time now this is directly correlated to the number of moles are the amount of solid that is actually undergoing a reaction that is the amount of solid that is undergone the reaction at a certain time. So, now, if at r equal to capital r so the ash is now present.

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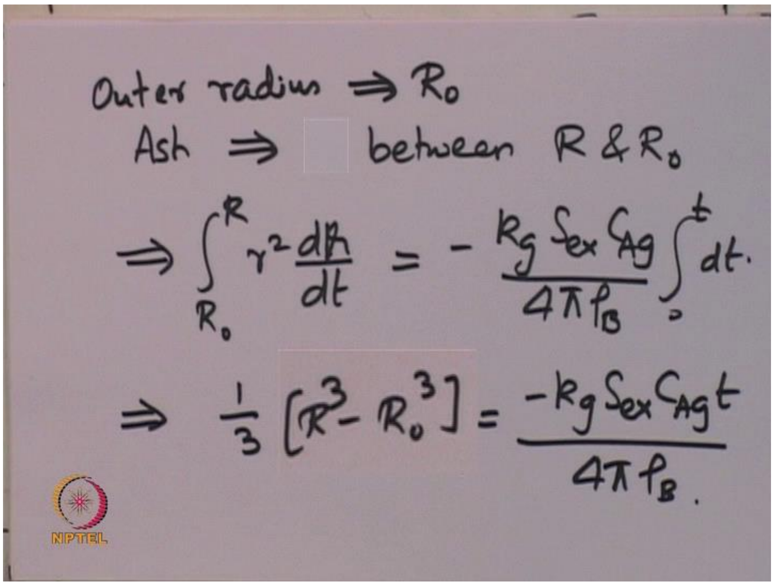

Outer radius $\Rightarrow R_0$

Ash $\Rightarrow$ between R & R_0

$$\Rightarrow \int_{R_0}^{R} r^2 \frac{dR}{dt} = -\frac{k_g S_{ex} C_{Ag}}{4\pi \rho_B} \int_0^t dt.$$

$$\Rightarrow \frac{1}{3}\left[R^3 - R_0^3\right] = \frac{-k_g S_{ex} C_{Ag} t}{4\pi \rho_B}.$$

So, the if the we assume that the outer radius of the core is r naught and if the ash is actually present ash is present between r and r naught between r and r naught. We can now integrate these expressions between r naught and r dr by dt and that should be equal to minus k g divided by rho b into integral d t. So, that is the … So, to now this integration will provide integration will now provide an expression for finding what is the radius of the unreacted core as a function of time.

So, integration suggest that it will be 1 by 3 that is equal to to rho b. So, this expression provides a relationship between the radius of the unreacted core as a function of time. So, if that is if the if the diffusion in the gas phase is actually controlling the overall reaction overall conclusion. Then we can find out how the unreacted core actually decreases in size as the reaction proceeds.

So, what we have seen in today's lecture is essentially introduction about the different what is the fluid solid non catalytic system and what are the different modes. Based on the size of the I based on the change in the size of the solid core that is participating in this fluid solid non catalytic a heterogeneous reaction. And then we looked at 4 different models the programs have been and the shrinking core model a description of these 2 markers. And we attempted to aborted the issue we have we have attempted to write the balance in order to find out what does the a size of the unreacted a solid core as a function of time for a shrinking core model when the diffusion in the gas phase is actually controlling.

Thank you.