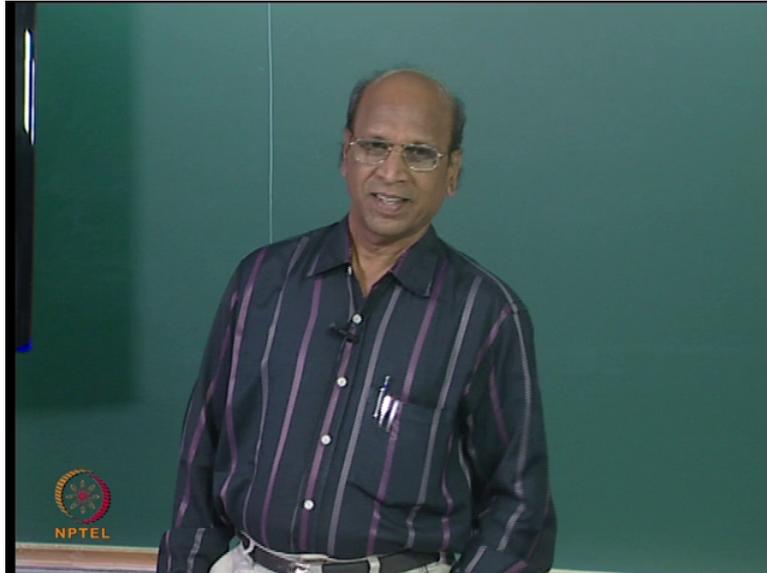


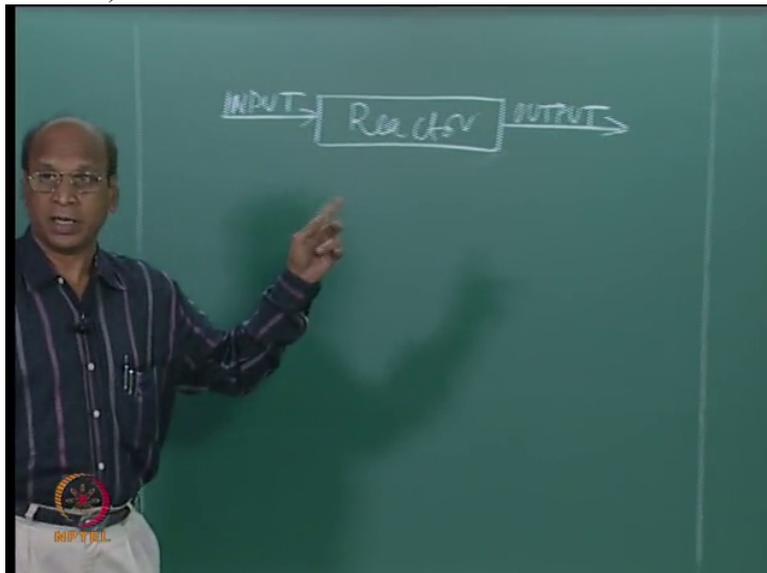
**Chemical Reaction Engineering 1 (Homogeneous Reactors)**  
**Professor R. Krishnaiah**  
**Department of Chemical Engineering**  
**Indian Institute of Technology Madras**  
**Lecture No 07**  
**Homogeneous and Heterogeneous Reactions Part 1**

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Ok, so in the last class we have been discussing about that beautiful diagram. I will draw it again and I have to draw many, many times. Reactor, I think by the end of this course, you will all by heart this, output and it is not a bad diagram.

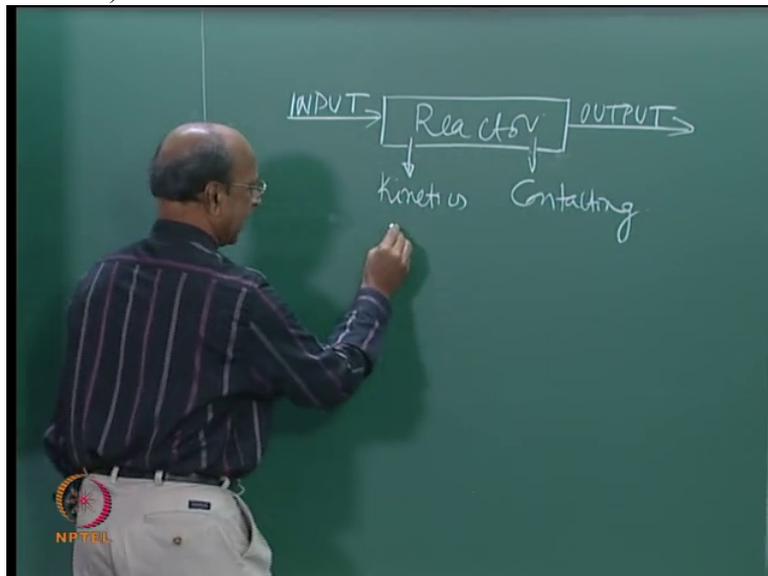
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Definitely if you remember this diagram you will know the entire picture of C R E, chemical reaction engineering, right. So that is why you have to remember this.

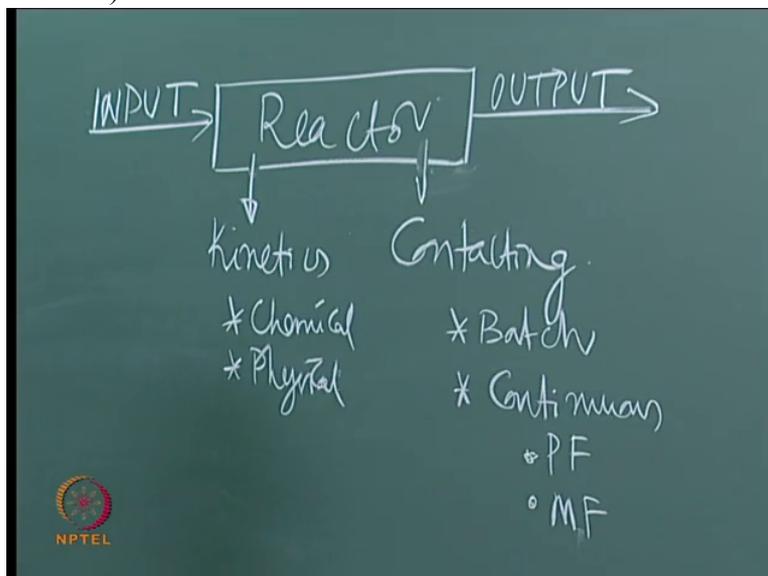
Ok this is kinetics. And here we have contacting.

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In kinetics we have again chemical and physical. And in contacting we have batch, continuous and in continuous we have P F and M F, Ok. Yeah I think P F means plug flow and M F means mixed flow, for those who have not, who are not familiar with this notation,

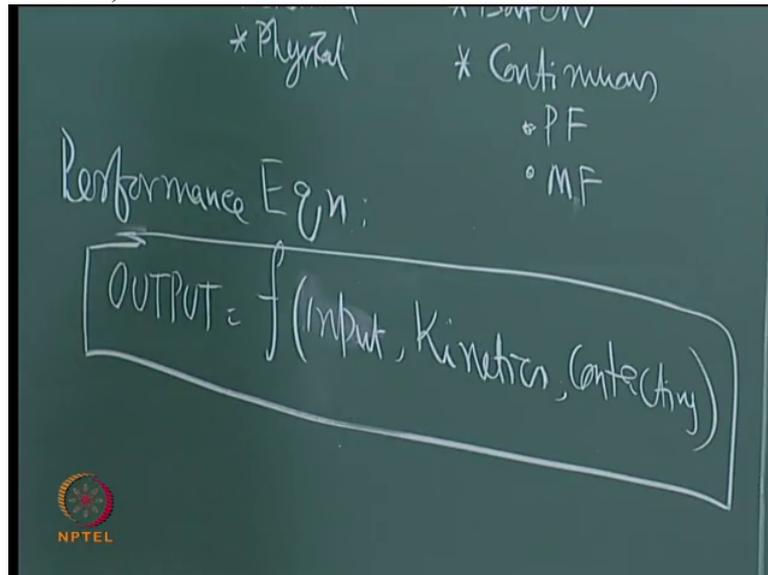
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Ok.

So then the performance equation, equation is given by this output is a function of kinetics, no, first input yeah, input, kinetics and contacting. Yeah, so this is the performance equation. Yeah, in fact this

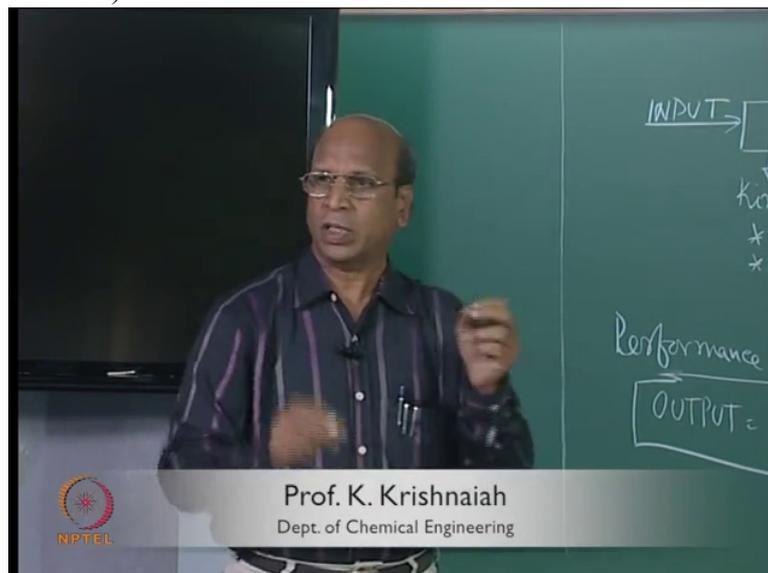
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tells us there are four variables, Ok. What we should know is kinetics which gives you a rate expression.

So that is why, it is no way different than you know biochemical reactor or normal chemical reactor because if you are able to get a particular rate in biochemical reaction like Monod's rate, and they are very lucky. They have only two rates, right? Either Monod's or Michaelis-Menten, right? And slight variations of that. You know in the denominator, numerator you add

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one term or remove one term you will get different forms of those two rates only.

But whereas in actual chemical engineering there are many, many, many forms of rates, Ok. So you have this kinetics giving you a rate expression, a rate and contacting will tell you what kind of reactor you have to choose. And fortunately for us, we have only three reactors, three reactors. Ok (laugh), yeah

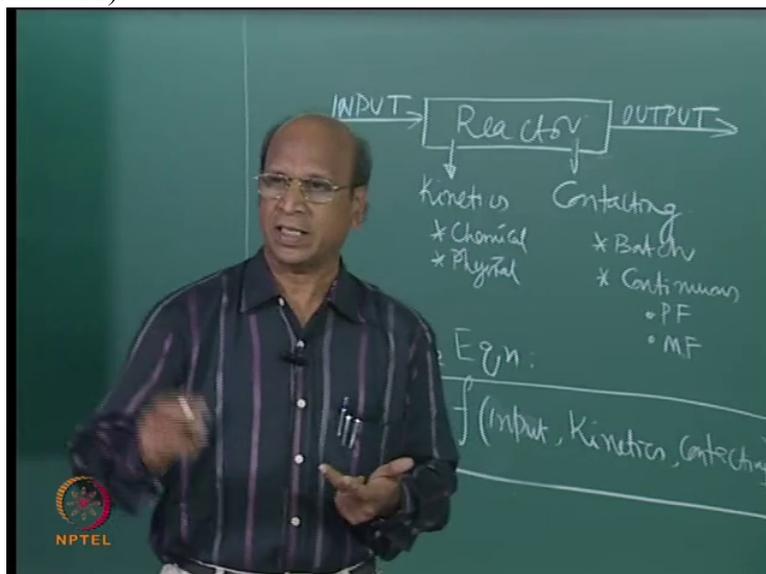
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three reactors.

So one is batch reactor and you have two continuous reactors,

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ideal reactors by name plug flow and mixed flow. If you are able to understand the meaning of this contacting, what is batch, what is plug flow, what is mixed flow, when do you use

batch, when do you use continuous, that means lifelong you have all the information with respect to reactors.

Only variation comes if they are not ideal, what is that? You want to know. What is that extra information that comes into picture? Ok that is why in my opinion, contacting is much easier to understand and also to use all the time whereas kinetics much, much difficult, right.

And I do not know how many of you really understood what is the meaning of chemical and physical? What is the meaning of this chemical and physical? Why did you write there, what do you mean by physical kinetics? What do you mean by chemical kinetics?

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(Professor – student conversation starts)

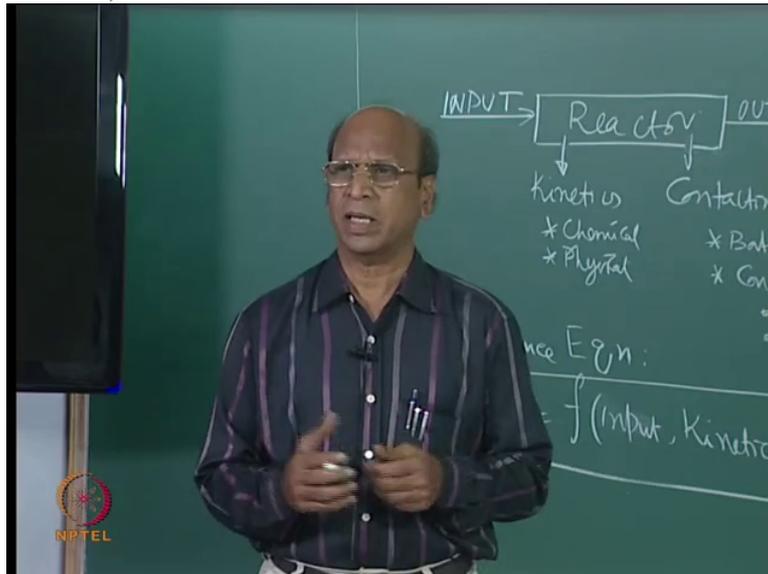
Student: Reaction rates at mass transfer

Professor: Who is talking? Yes, right? Reaction rate at

Student: Mass transfer.

Professor: Where does that come? Where does mass transfer come

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in chemical reaction rates?

Student: Reaction

Student: Chemical may diffuse only...

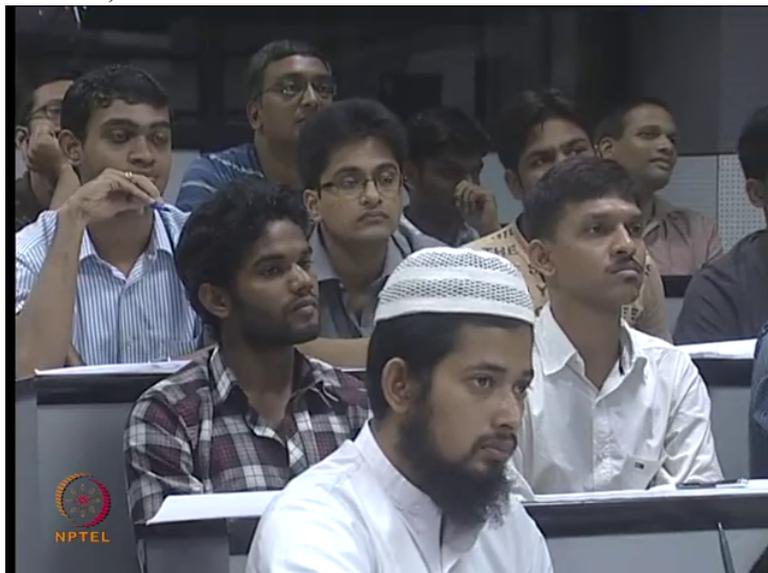
Professor: Where? Where do they diffuse? Where?

Student: Heterogeneous reactions

(Professor – student conversation ends)

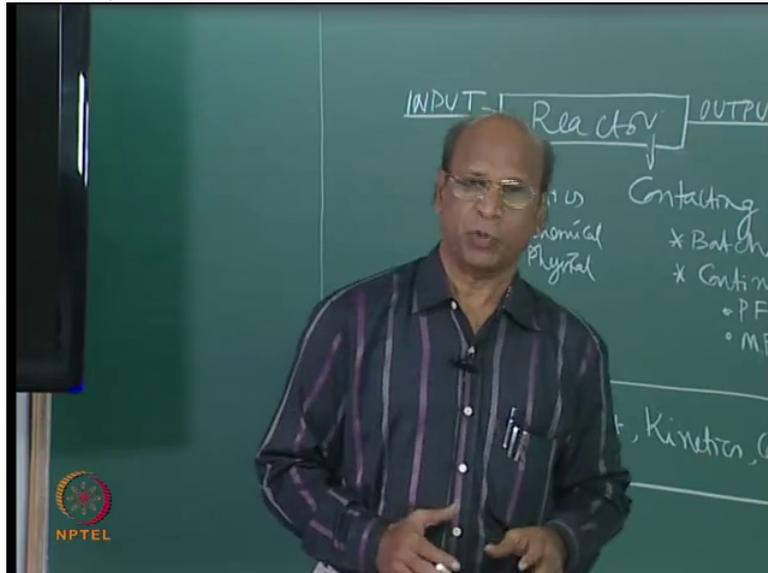
Heterogeneous

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reactions. Right, in all heterogeneous reactions you wrote very nicely that question, everyone wrote

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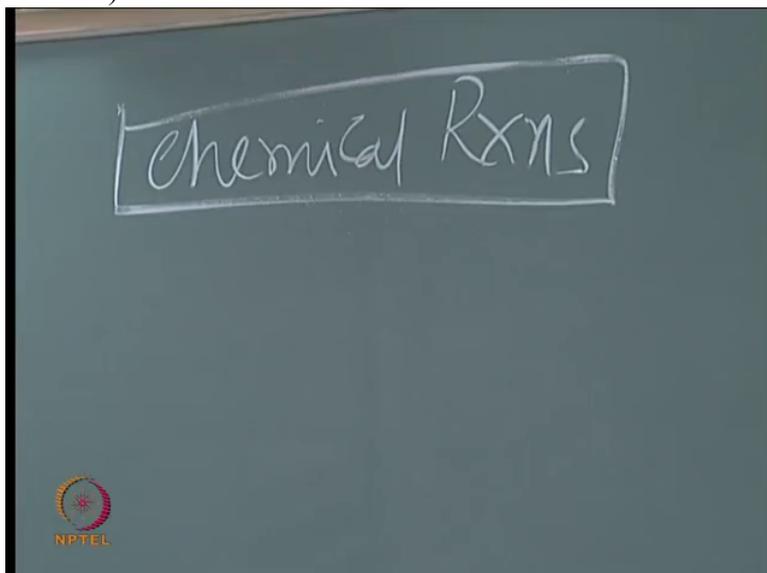


uniformly, right. Ok, heterogeneous reactions and homogenous reactions. What is the extra information we require in the heterogeneous reactions when compared to homogenous reactions? That mass transfer that is extra step.

Ok, but in fact that is much more difficult because for every reaction you have to visualize how that reaction is taking place. That we will discuss a little bit later. But now first the contacting pattern is easiest so I thought I will do first contacting but before that when you are writing an equation for either batch or continuous reactors, either this or this, we need a rate expression.

So that is why we have to come back to kinetics again and then question this chemical and physical, these things will come in homogenous and heterogeneous reactions, right? So we can now divide these chemical reactions, now short form,  $R \times n$ , like Action TV no you have  $A \times N$ , so like this here, reaction, right,

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R x n means reaction, Ok.

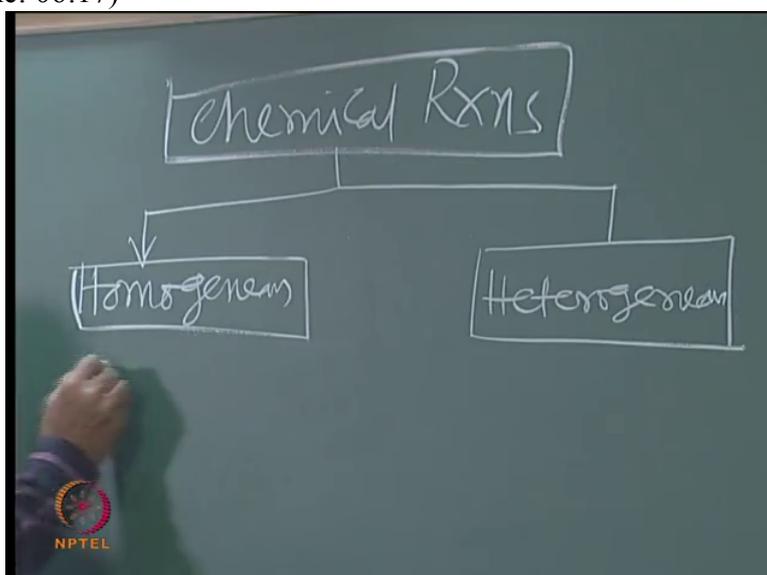
Now chemical reactions can be divided into homogenous and heterogeneous, Ok. Now we have to identify homogenous. How many phases you have, homogenous means what is the definition you already know. You are the experts. You should have one phase, Ok. Everything should be happening in one phase. So how many phases you have?

(Professor – student conversation starts)

Student: Three

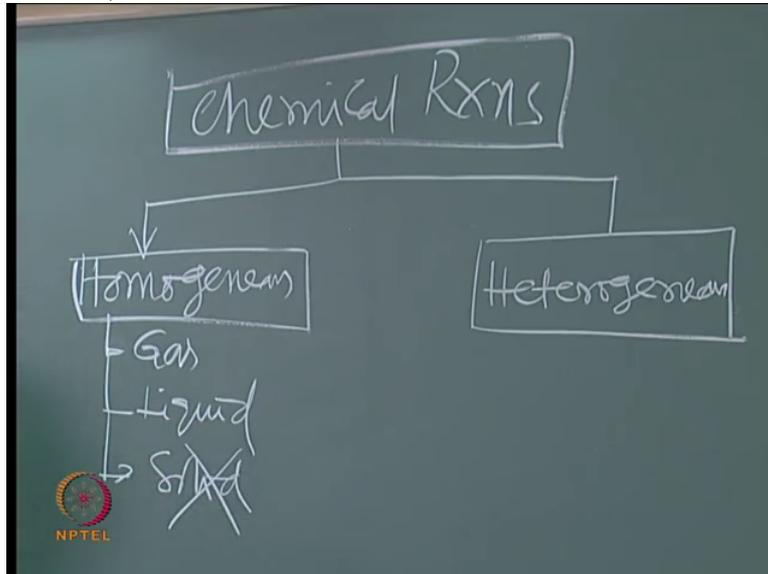
Professor: So shall I list all these three here?

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We have gas phase, Ok, a gas phase and then liquid and solid, Ok. Yeah. This is never called as homogenous,

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right. Because what is the meaning of homogenous when you are talking in chemical reactions?

Student: density

Professor: For solid also density remains constant?

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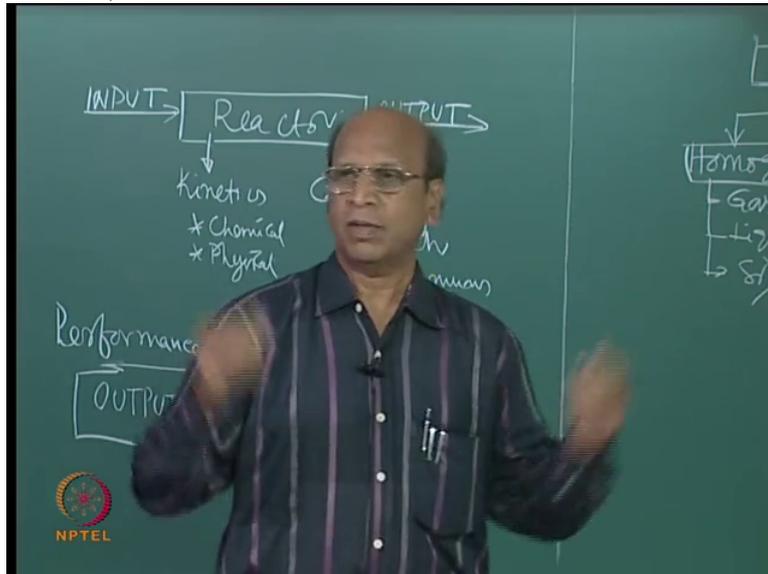
Student: No

Student: Uniform

Student: Conservation

Professor: This is the problem no, but homogenous we know, but beyond that when you ask,

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we do not get any answers most of the time, Ok. And what is that requirement in homogenous requirements? Why do we say that, Ok it is homogenous, homogenous means single phase but so what? What is happening in that phase?

Student: Reacting

Professor: Reacting?

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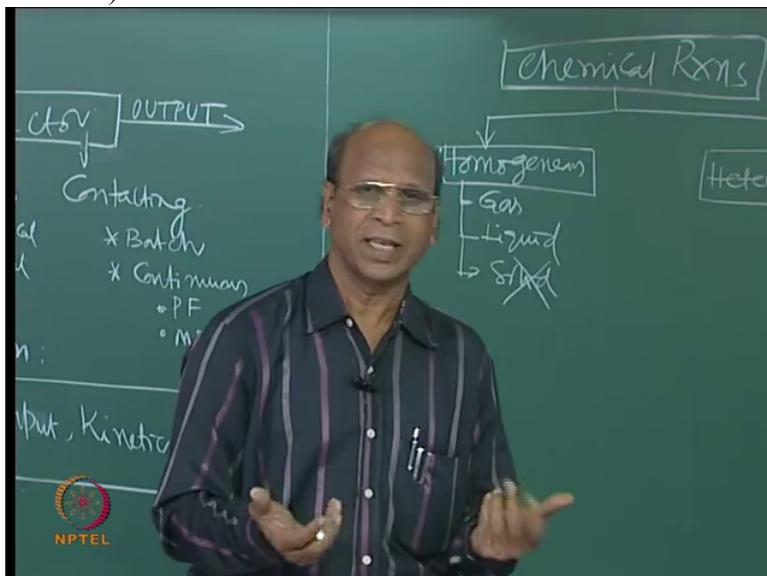
Student: Molecules are

Professor: Molecules are?

Student: Reacting

Professor: Everywhere, heterogeneous also molecules are reacting. Otherwise who will react?  
You will react, I will react?

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Student: (laugh)

Professor: (laugh) We react in a different way; that is different. Ok molecules only definitely react, Ok but still why do you call it is homogenous?

Don't get disheartened, I mean we are only just learning. So that is why you should not get, next time you should not say, no this man is laughing so that is why, no, no, it is only for joke. That is all.

(Refer Slide Time: 07:45)



Yeah. Molecules definitely react but then actually what is the requirement for homogenous phase?

Student: Properties will remain same.

Professor: Yeah, still what is the meaning? Properties, Ok, they are remaining same, so what?

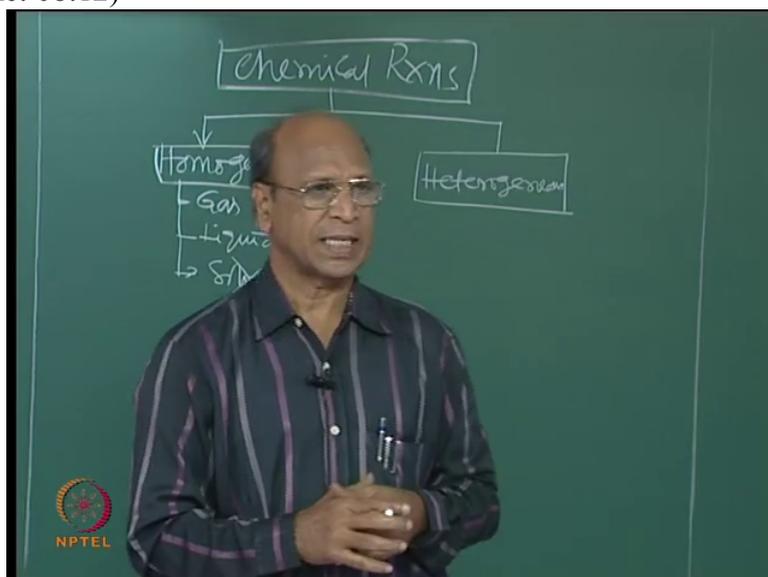
Student: So determining kinetics will be much more easy.

Professor: Why? Properties remaining same...

Student: At one location it will be different and at some other location it will be different.

Professor: That comes as mixing, but I think

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you know yeah, properties same means I think we are talking about concentration same throughout, but I think... See the basic requirement in homogenous phase is that molecules should be readily available for reaction, right?

(Professor – student conversation ends)

So that means if I have A and B together in homogenous phase, A need not search for B. B need not search for A. Both of them are there very near so they come together and then collisions and all that we can imagine no, then immediately you will get the reaction.

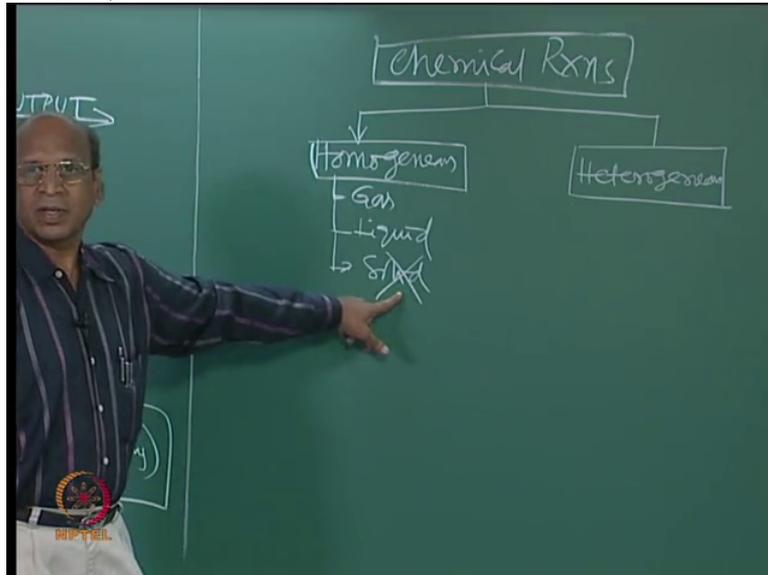
So that is why the basic requirement for homogenous phase definition is that you have the molecules together and sufficient amount whenever A wants to react with B, B wants to react with A. It is not only that. Many times you will have A decomposing to some other reaction.

So that means all the A molecules should be just present there and when you create this reaction environment they should be able to easily react. That in the other sense, the

molecules of a particular reactant in that phase should be freely available. There is no extra effort that is required for the reaction to take place, right.

Ok, so then that is what is the definition and that cannot happen in solid phase.

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Ok and even though you take the purest form of solid, the molecules are not able to freely move. Ok. So that is why this is a question mark always whether we have to call solid as homogenous or heterogeneous, Ok

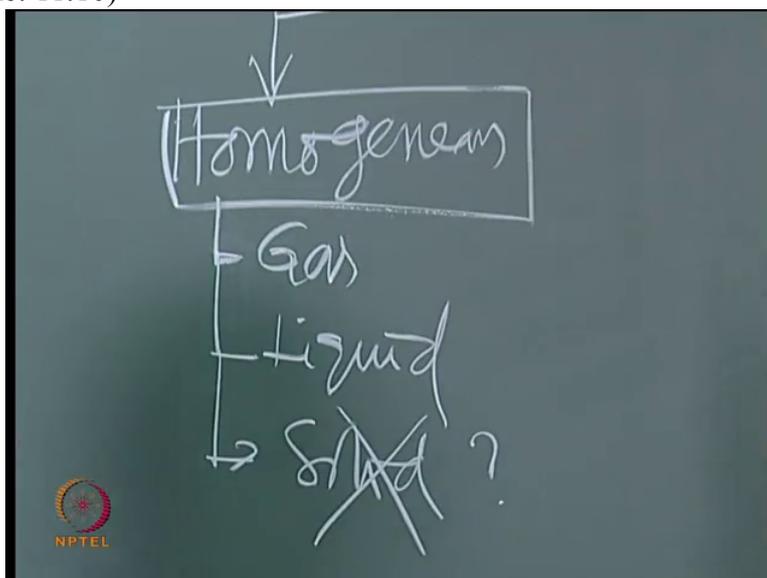
But most of the time, we never get purest form of solid anywhere so that is why when the molecule wants to react with another molecule, that has to diffuse extra, Ok, within the solid itself. So that is the reason why when compared liquid and gas where the molecules are very free to move.

I mean the kinetic velocities are 300 meters per second, 500 meters per second and what is your diameter of the reactor? Maximum 3 meters and that is moving 500 meters per second, the molecules, particularly gas phase, so you see 500 meters means from here to your hostel in 1 second it goes. Can you go? If you are able to go, when you are hungry you may go. Ok, 1 second, half second also. So that much faster, that means you can just imagine how easily they are available.

Whereas solids by definition, they would not move. The molecules do not move. So that is why you have to apply more temperatures where more energy comes for the molecules, they try to move and then you know that self-diffusion is there. So then other molecules will come together and then both will react, all that information is required, all that steps are required.

So that is the reason why normally we do not call them as homogenous. That is why all the time we have gas and liquid as heterogeneous,

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I mean homogenous systems. Where, that means there is no effort extra required at all for the molecules to require, except temperature you are providing, sufficient concentrations you are providing so that anytime the reaction can occur. That is what the definition of homogenous reaction is.

So I want to tell these basic things in a number of times, the reason is that those are the things which we have to understand. We know only the meaning of homogenous but beyond that if you ask one more question I think if you are not able to answer means that is not the knowledge.

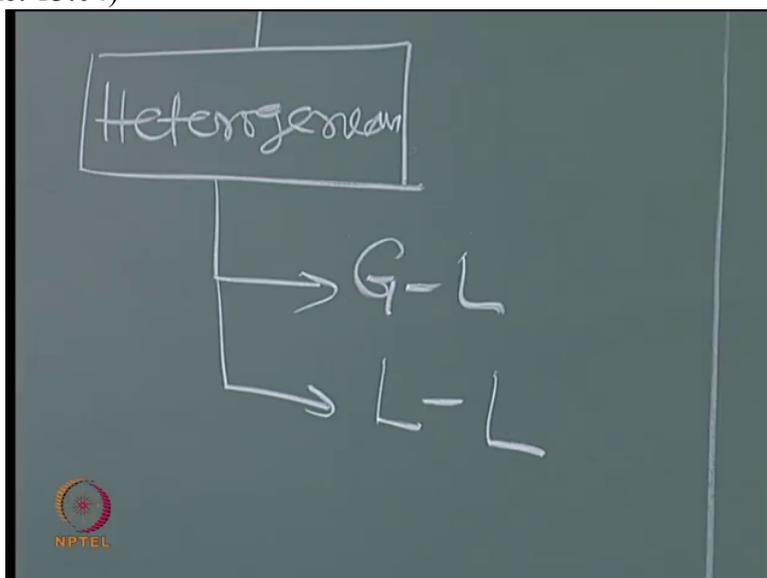
That is only the parrot knowledge where parrot repeats, homogenous, homogenous, homogenous, ten times if you tell, throughout the life it will just repeat. If you ask the parrot, tell me Ok, explain what is the meaning of homogenous, it cannot. So we should not become parrots. So that is the reason why extra information is required for us.

So the basic requirement for homogenous phase, when you say that I have a homogenous reaction is that absolutely there is no mass transfer limitation, molecules are freely able to move and at any time if there are two, A and B these molecules are easily available to each other for the reaction to happen. Ok. So that is what is homogenous.

And heterogeneous, this we will remove now, we have more than one phase, right. Yeah, so that means now we have totally 3 phases. The combination of all these 3 phases will give us the overall number of types of, yeah, the overall types of reaction rates, the reactions, Ok.

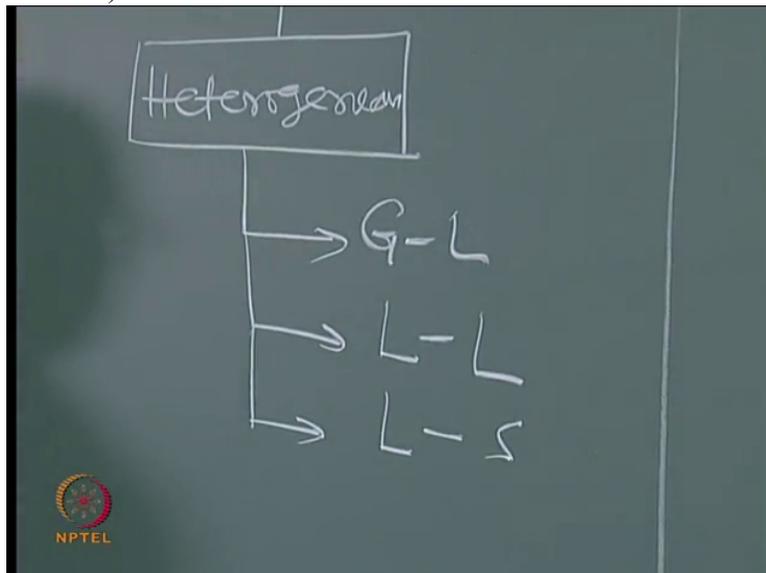
So I do not know whether you have understood or not. We have three phases. Combination of these three, that means we have gas, liquid, solid, right three. So first we will write here, gas-liquid is one combination. And then liquid-liquid is another combination,

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right. And then we have liquid-solid is

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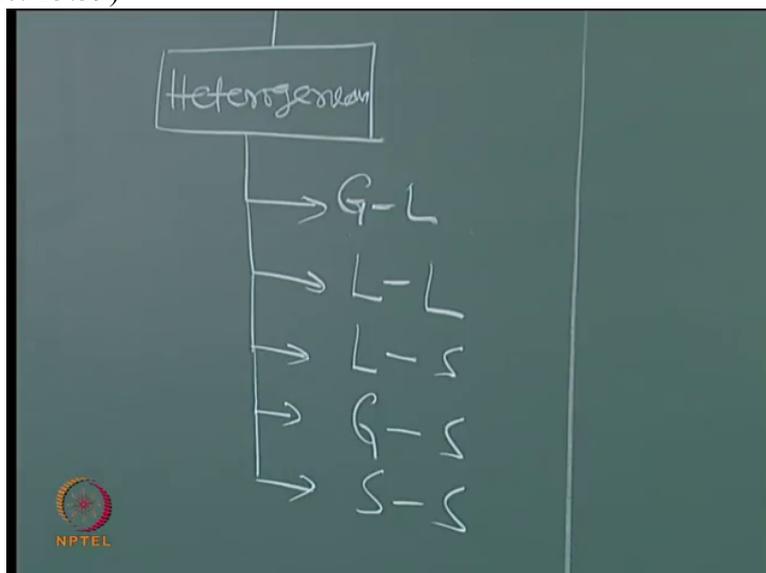
another combination, yeah. So then we have, another combination is gas-solid.

(Professor – student conversation starts)

Student: 0:13:23.4

Professor: Yeah, yeah, yeah, yeah, I will come; I will come to that, Ok. So then gas-solid is another combination. Then what is the other one you are telling? Solid-solid. Is there any other combination?

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Gas-gas there is no combination because gas-gas molecules are so fast, because I have written liquid-liquid no, so he is adding gas-gas.

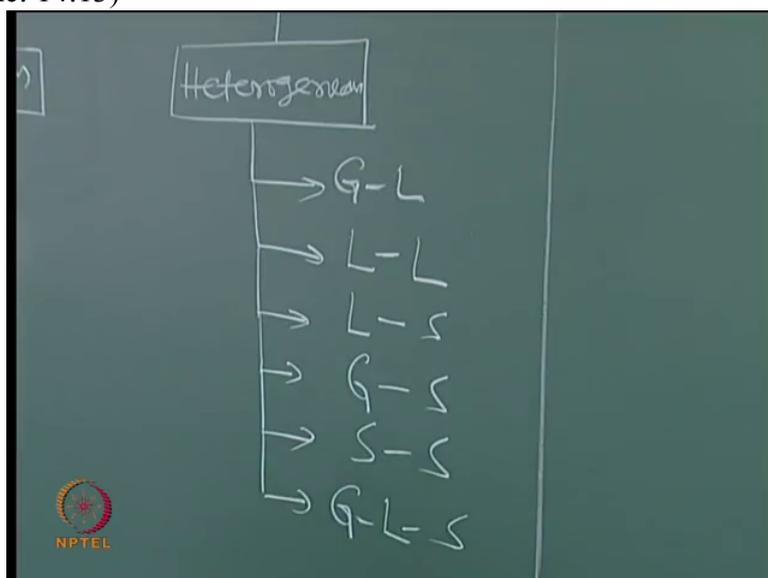
Student: (laugh)

Professor: (laugh), we have now added liquid-liquid, gas-gas, and solid-solid also, Ok. Yeah gas is always homogenous because that is very, very free, happy to move. Ok, that is why that will not come.

(Professor – student conversation ends)

And yeah, gas-liquid-solid. Now usually I will give the first exercise, first assignment

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is this. Now find out under each category, under gas-liquid reaction heterogeneous system, five, minimum five actual reactions. You cannot even tell one. Gas-liquid systems, can you tell one reaction? Actual reaction I am talking.

See how much time you are thinking. Yeah I know where to hit exactly (laugh). That is very bad. Ok. Now tell me at least liquid-liquid reactions. We do not know. At least liquid-solid reactions. There are few, which is easy for you to, yes, yeah, very good, bleaching most of the time, right.

That means you take a solid, for example if you want to remove purest form of copper you take copper ore, add sulphuric acid or HCl and then now you will have copper sulphate, I told copper no, if you take sulphuric acid, copper sulphate, now if you take copper sulphate to electrolytic cell and then separate  $\text{SO}_4$  and separate Cu, you will get the purest form of copper which will get deposited on one of the, you know, yeah, cathode or anode, yeah. Ok, yeah.

So that is what? You will have this one. Gas-solid systems? Many. This you should be able to tell. Burning of coal, copper oxide formation, everyday you see rusting. Yeah, rusting  $\text{Fe} + \text{O}$  giving you  $\text{Fe}_2\text{O}_3$ . You leave your cycle there and before you go, after M Tech you will see only rusted cycle. Most of you would have purchased good cycles, no? New cycles.

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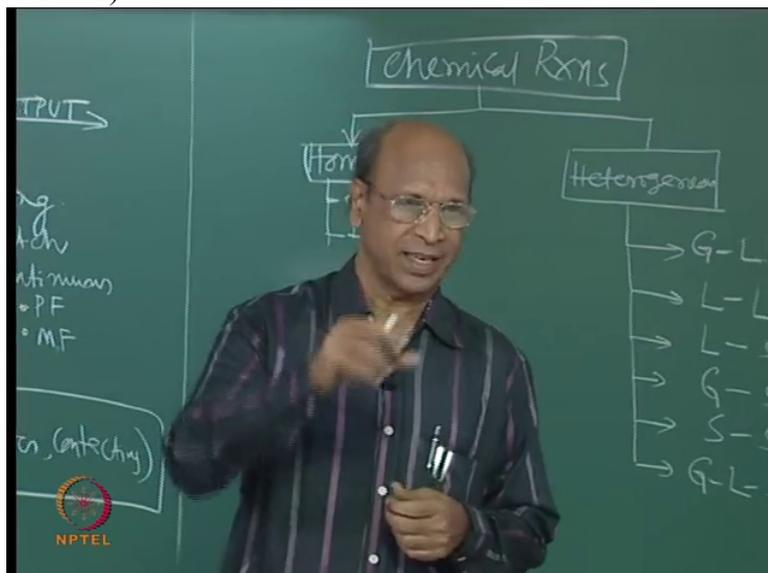
Yeah, lock them properly. In IIT, all new cycles will go once, at least once (laugh).

(Professor – student conversation starts)

Student: (laugh)

Professor: So that is why I think you buy most costlier than cycle,

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keys locks, cycle now, how much is cycle now?

Student: Four thousand

Professor: My God! You know when I joined here, P h D, how much I have purchased, can you guess?

Student: 500

Student: 400

Professor: Good guess, 400 (laugh). Just 400 I purchased. At that time also, no thefts, happy. No one was stealing our cycles, cycles used to be there. But nowadays I think, smart people you know, so what else do they do? I think, doing this kind of things, they think it is very 0:16:47.0, very, very smart. Ok anyway.

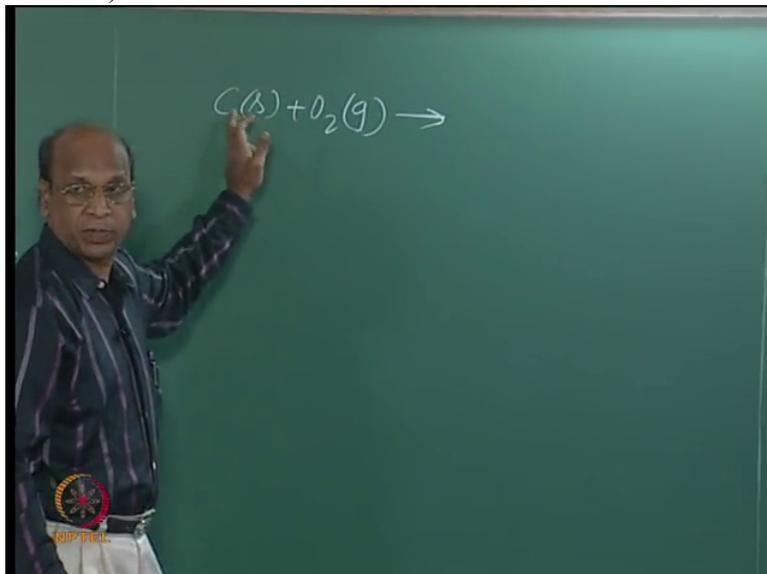
(Professor – student conversation ends)

So rusting of iron and all that we will come. But what you told all these things, examples like coal combustion, carbon plus oxygen giving you  $C O_2$ , I mean if you assume only that reaction is present, all those reactions are called non-catalytic reactions. What is the difference?

Both the reactants, carbon plus oxygen, both of them are reacting, are participating in the reaction to give you  $C O_2$ . But now you see, I will give you an example, so that kind of, even  $F e O$ ,  $F e$  solid plus  $O_2$  oxygen will give you  $2 F e O$  that I will write now. I think I can write here.

C solid plus O<sub>2</sub> gas, better write these things, earlier you were not writing the state of the

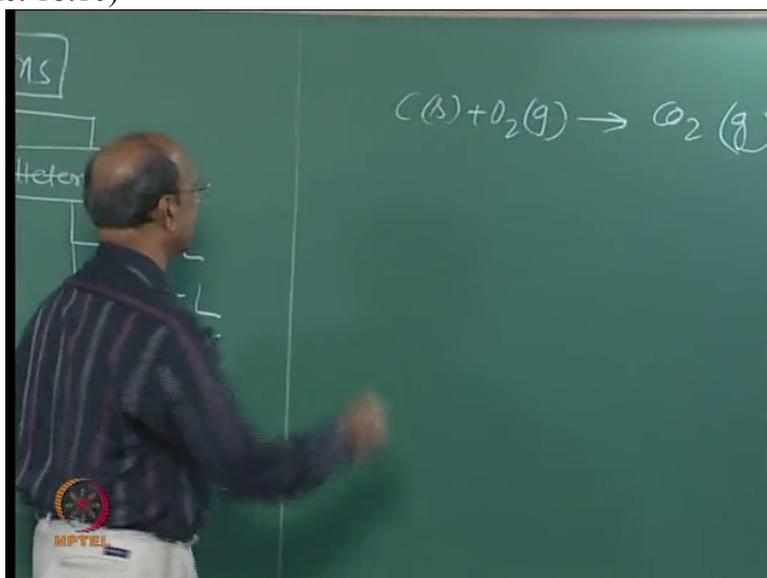
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reactant. So better write now so that you will immediately know whether the system is homogenous or heterogeneous. Because you have now two phases. If I do not write s here, do not write g here, you do not know what is that. You do not know which phase they are.

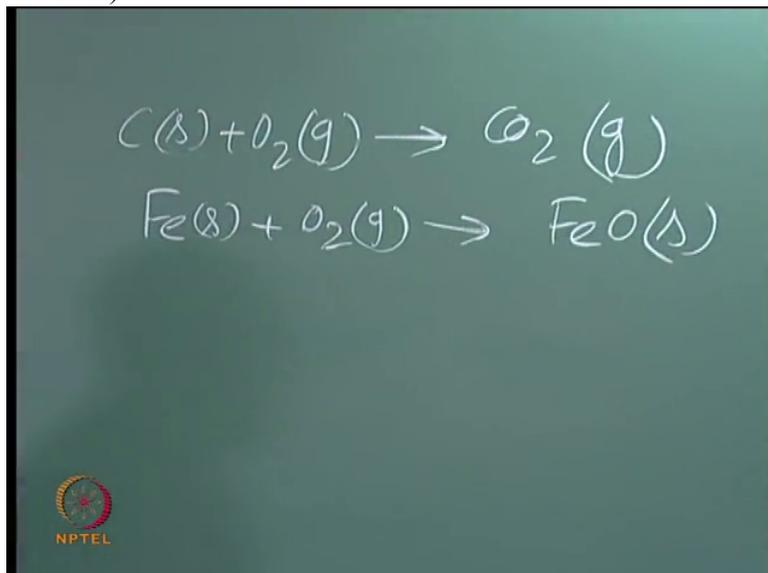
Of course carbon and oxygen we know but some other chemicals you go, we do not know that. That is why better write that. If you do not know you have to find out and write. This is C O<sub>2</sub> gas. This is non-catalytic

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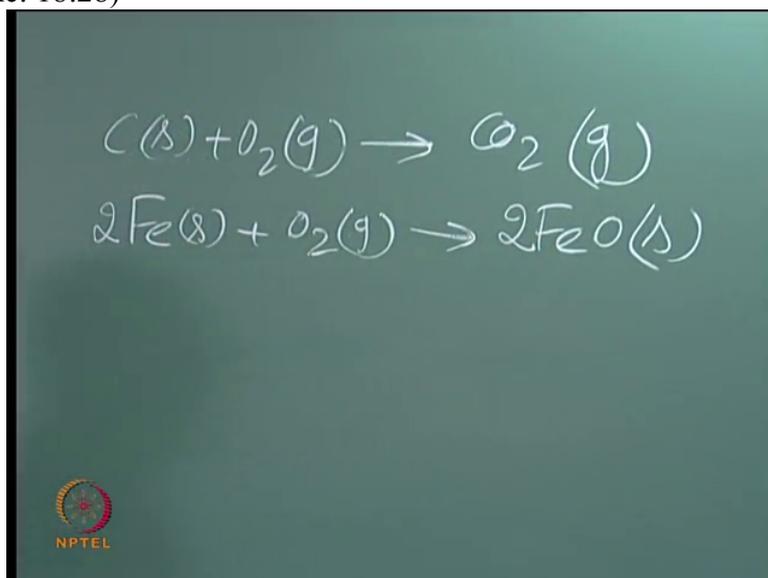
reaction. And also I have Fe solid plus O<sub>2</sub> gas giving us FeO solid,

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correct no? Yeah so now it is balanced, 2, 2 so that is

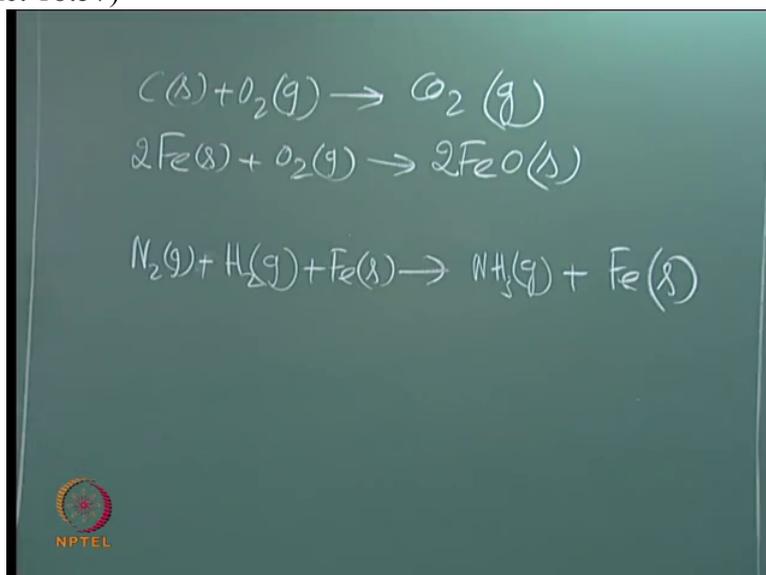
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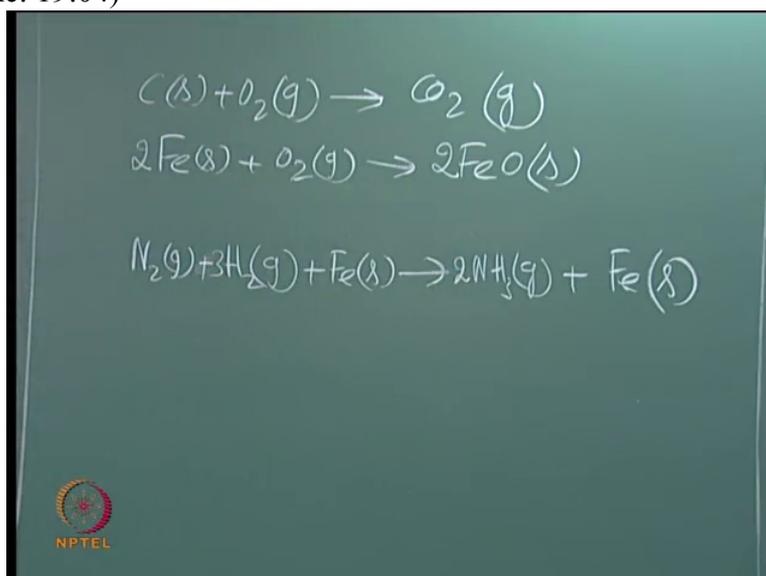
And now the same Fe, I can also use in other reaction, for example N<sub>2</sub> gas plus H<sub>2</sub> gas  
yeah plus Fe solid giving us NH<sub>3</sub> gas plus Fe solid, right?

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Yeah. So now I have to balance again this one. This is 2, this is 2, this is 3.

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What is the difference between this and this? Here also I have F e. Here also I have F e.

(Professor – student conversation starts)

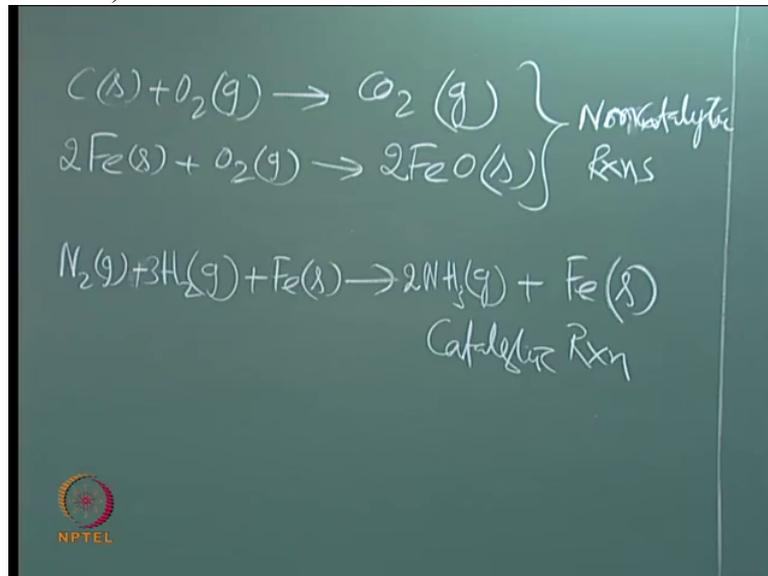
Student: Catalytic reaction

Professor: Yeah. Here it is not actually participating in the reaction and getting transformed to something else but it is retaining its iron form as it is, only thing is it helps the rate of reaction to increase, right. Yeah.

(Professor – student conversation ends)

So that is why this is a catalytic reaction, this is catalytic reaction and these two are non-catalytic reactions, non-catalytic reactions, good, very nice, yeah.

(Refer Slide Time: 19:51)



So this we have to first identify. Because the design of catalytic reaction is totally different when compared to the design of non-catalytic reaction, right?

But here catalyst is there. You have packed bed for example. That one of the examples we give is packed bed. Ammonia they always use packed beds only. All iron is loaded in this reactor and then hydrogen and nitrogen it is sent continuously, so you will get continuous things and most of the time this will not get deactivated, you have deactivation of catalysts so that is why, for lifelong you can run that if you do not have deactivation.

That is why packed beds are very good, in the sense that in packing, when you have packed beds the solids are not moving. When you have movement of solids then you have lot of problems, Ok, how they move, where they move, and when they are moving they are also rubbing towards the walls, so after some time, 10 years if you run walls may get eroded, thickness may go, then it may burst, all these things are there.

But if they are not moving, happily sitting there, then, that is why packed bed is called workhorse of chemical industry, workhorse. You know there are two types of horse, workhorse, running horse, Ok. Running horse will be useful where? Only in race courses, Ok and they run only, may be how many minutes, I do not know. I have never gone there.

Anyone has gone for races? No, nothing wrong I say. To go and see also, no problem. How many, 1 round I think, 1 round or 10 rounds I do not know how much, but maximum, you take that a maximum half an hour it runs. And you know preparation for half an hour run? 1 year. Good amount of food, some injections, many things they give. So it is not profitable to industry.

Because we need a horse which will work all through, not that half an hour and then you know, the remaining 395 days, no 365 days minus half an hour. So it will be eating, eating, eating, eating all the time. That is waste of time for us, waste of money. But we need workhorses where all the time they work and in-between they also eat, right?

So that is why the chemical industry, the packed bed, without any problem all the time it works. That is why the name is given for packed beds as workhorse of chemical industry, Ok. So that is a very nice name, Ok. So that is why in the catalytic reaction what happens is the solids are there all the time and you have to find out only what is the total amount of solids in the reactor.

Ok, based on, that is why your design will be to find out what is the total amount of catalyst that is required. Whereas here I do not have  $F_e$ , at the end I do not have  $F_e$  but it will become  $F_e O$ , at least this is becoming a solid. But you see here, I start with solid and I start with gas, now everything is gas. What volume you calculate? Is it solid volume or gas volume?

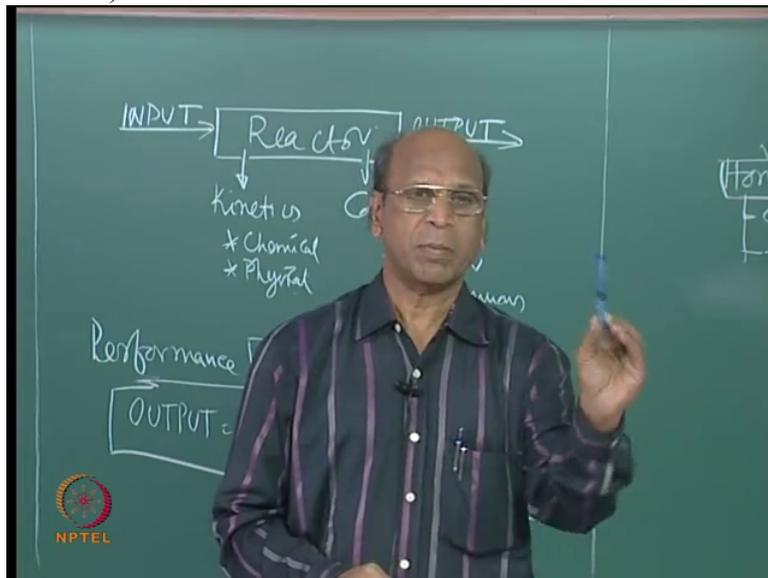
Yeah, we will see, it is not gas volume but...that is why the design of non-catalytic reactors and catalytic reaction is totally different or reactor totally different. And now we extend our definition, these are chemical reactions. The same thing is duplicated, if I write here chemical reactors, that means wherever reactions are taking place, you can call them as heterogeneous chemical reactors, right?

So that means I may have G-L, gas-liquid reactors, liquid-liquid reactors, liquid-solid reactors all combinations. And this one, g-l-s is called as slurry reactor. Most of the time the solids are used in the form of slurry, and even you have liquid and put solids and you do not put you

know, 1 kilometer, 2 kilometer diameters. Ok. You will put only 10 microns, 20 microns, 30 microns; you know you have the idea of microns? Yeah.

How much, I do not have hair to say, but how much your hair thickness? Point 5 microns. So that is why, anyway as engineers you better have, you know that kind of estimation in the mind. Excellent, what he has done is really good. We should have that kind of estimates. Like for example if I ask

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what is the diameter of this pen? What is the diameter of this pen?

(Professor – student conversation starts)

Student: 1 centimeter

Student: Half a centimeter

Professor: Yeah 1 centimeter, length?

Student: 12 centimeters

Student: 20 centimeters

Student: 12

Professor: Yeah may be 10 to 12 yeah. That means you know 6 inches almost, Ok so like that, you know. For example when you are writing, yeah, the smokers, cigarette, what is the diameter?

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Student: Half centimeter

Professor: Half centimeter, what is the length?

Student: 3 centimeters

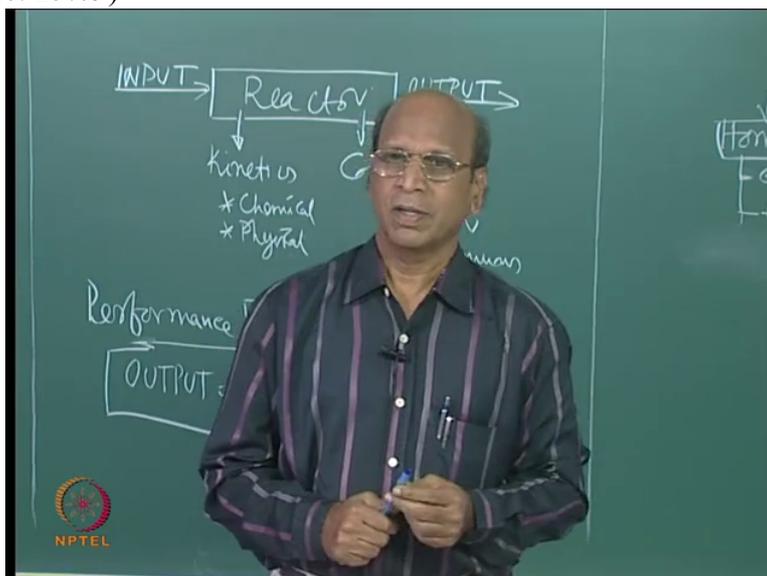
Student: 2 inches

Professor: In fact, that is non-catalytic reaction.

Student: (laugh)

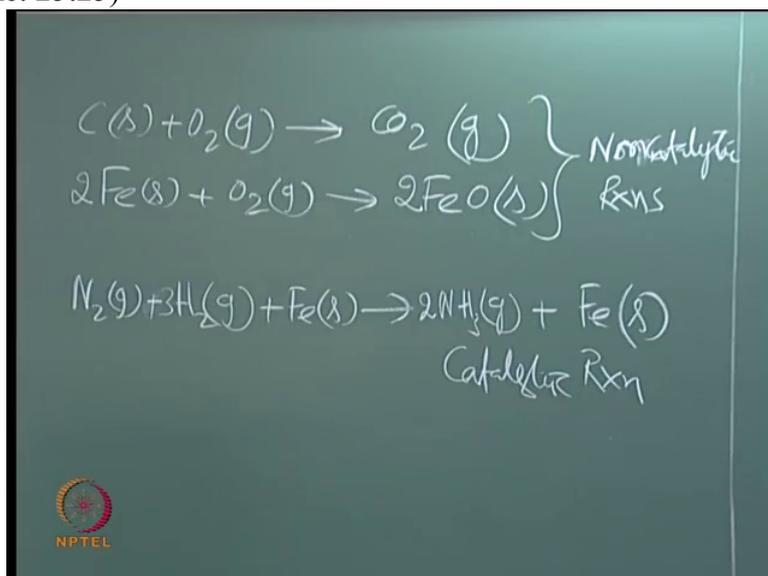
Professor: Correct, no? You are burning tobacco,

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Ok and that is becoming, carbon becoming ash, yeah. Carbon also becomes ash if you have some other; you know silica and all that. So this also becomes ash, no? Every time you like this, it falls, all that. So you can also calculate from non-catalytic

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reaction rates what is the time required for normal smoking of a cigarette. Normal smoking is simply taking and then taking one breath or so. But some people 0:25:36.50 (inaudible sound) (laugh)

Student: (laugh)

Professor: You know, for them the rate of reaction is very, very high (laugh). Why it is very, very high? Not, you know. There is some step there. In fact there is a mass transfer step coming, I do not know for the...when I am doing 0:25:56.6 (inaudible sound) what I am trying to do?

Student: Inhaling

Professor: I am sucking the air; you know the oxygen will come through the pores, because it is porous. You will not have solid, you know cigarette. Solid cigarette means you cannot, you know, smoke will not come. It should be porous. And the beautiful question is what is the porosity of the cigarette? Yeah, general knowledge

Student: (laugh)

Professor: (laugh) What will be the porosity?

Student: 0:26:23.7 10 power minus 6.

Professor: (laugh)

Student: (laugh)

Professor: Unit size, meter cubed or kilometer cubed?

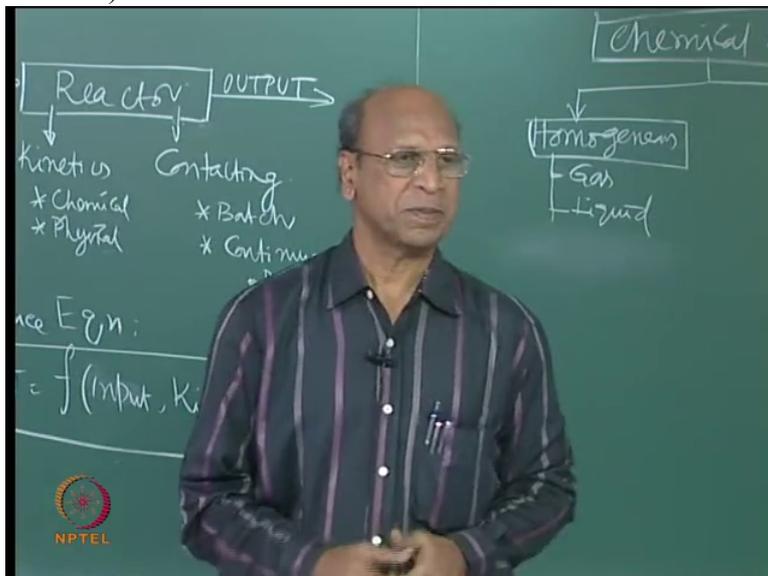
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Student: 0:26:34.3

Professor: Just guess? No guessing. Chemical engineering, no guessing. (laugh). That will be around 50 percent.

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It is a packed bed, I say. Yeah, it is a packed bed, simply.

(Professor – student conversation ends)

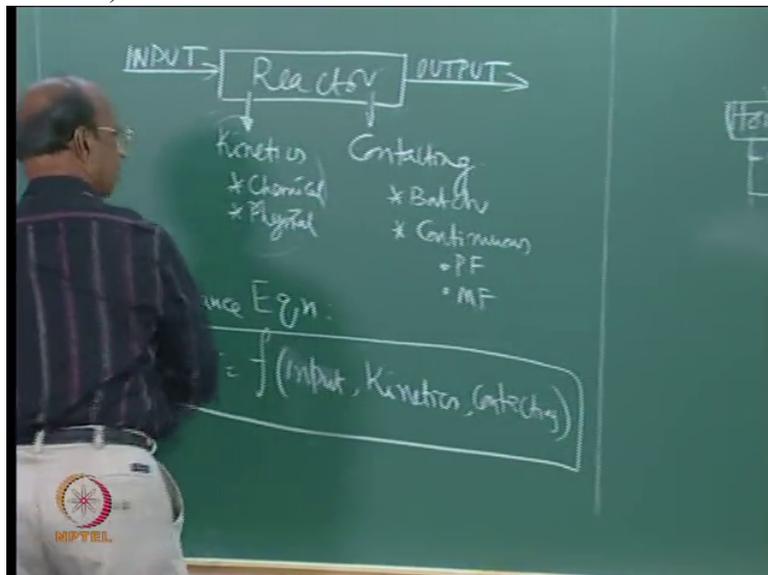
Because if you make the porosity point 2, point 1, your lungs will go much quicker. Anyway they will go (laugh). It is only the time, it is only the time. Whether you choose 10 years or may be 1 year, so that is why the design of, you see, for everything there is wonderful design, no. Really for everything there is wonderful design.

And also to stop all that nicotine and all that, they will have another filter on the top. Actually that is bad for the lung, because it will extend your life a little bit but lung will go because that porosity is bad, you know the filter porosity, right? That may be only point 2, point 3 like that. So there you have to apply more pressure drop. The pressure drop across that is more. See all chemical engineering only we are talking. Even though we are talking about cigarettes.

So every problem you can convert into a chemical engineering problem. And then discuss about pressure drops, flow rates, mass transfer all that. So that is what, this person 0:27:48.1 (inaudible sound), like that he is doing, that means he is taking lot of oxygen, so burning rate is more. So cigarette is burnt very, very quickly. Right? So that is why the designs of non-catalytic reactions not because of cigarettes, the, when these two reactants are participating in the reaction the design is different where as in this case the design is different.

And, and this is also the reason why the rate of reaction is different here, the rate of reactions are different here. So for every reaction you have to find out rate of reaction for heterogeneous system. That is why I told you this portion is very, very difficult.

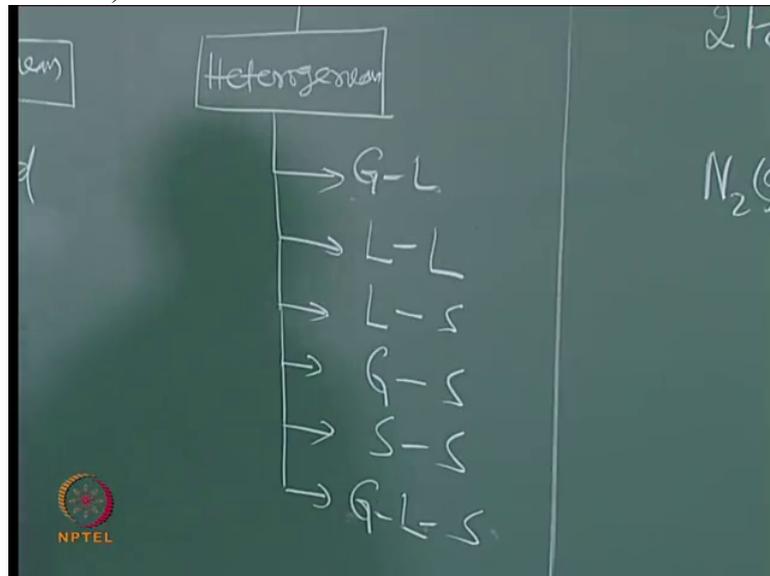
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Every reaction you have to derive an equation. Whereas whatever reaction you bring you have only 3 reactors, correct no? Any reaction you bring, any heterogeneous, any homogeneous or all, all three phases...

Nowadays biochemical engineers have actually four phases also. It is gas, liquid, liquid, solid.

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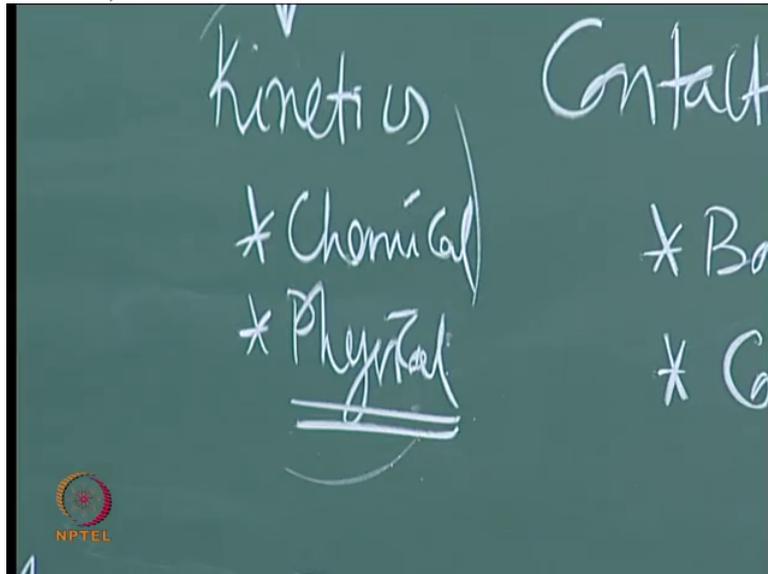
Ok, someone was telling no, that this immediately when I wrote this, someone was telling, sir, no, no, this is not correct. Liquid-liquid is homogenous. It is not homogenous. Yes, it is homogenous if both liquids are thoroughly miscible.

If they are not miscible, then definitely, like take for example, kerosene and water or some oil and water, in this oil, you have some reactant, and water is another reactant let us say. So now for the reaction to take place, the reactant in the oil should come to the surface, interface, Ok.

Similarly from water side, the reactant has to come or water itself if it is a reactant, that has to contact that particular reactant which is in the oil, then only the reaction, that means what is that? That extra step.

What is that extra step? Mass transfer. Not only mass transfer, even heat. So heat and mass transfer both should be present that is why we call this as physical reactions, I mean, you know physical steps that are required for chemical reactions.

(Refer Slide Time: 29:59)



Because mass transfer is a chemical step/step, physical step, and reaction also, sorry heat transfer also is a physical step.

So those are the two extra things that are required for the heterogeneous reactions, for the reaction, for the reactor to be designed. That information you require. Why? Because that information only tells me what kind of rate expression I have whereas in homogeneous reactions, what is the general rate expression, just guess one, first order rate for example, minus  $R_A$  equal to  $k$  into  $C_A$

(Professor – student conversation starts)

Student:  $C_A$

Professor: That  $C_A$  contains all the molecules. You have the concentration. How do you express concentration?

Student: Moles per unit volume

Professor: Moles per unit volume. So in that unit volume how many moles are there? In one mole how many molecules are there?

Student: Avogadro number

Professor: That's all, so that is the reason whereas that is not guaranteed in heterogeneous, the concentration, Ok.

(Professor – student conversation ends)

So that is why, unless Ok, let me give this example, I have this reaction, carbon plus oxygen going to  $C O_2$ , I keep carbon here and then next room we keep oxygen, where is the reaction? It has to necessarily contact. That is why the term contacting has come. And this contacting is very, very suitable for heterogeneous systems.

Because in homogenous there is no contacting in the sense that you know individual phases were not contacting. But here you have many, many possibilities. How do you put gas-liquid into the reactor? If it is batch both you put and then wait. If it is continuous...because you can choose either continuous or gas, yeah counter current, yeah, that is only possibility? Why not co-current? Is that only possibility? Why not cross currents? And beyond that we do not have any currents, Ok yeah.

So all these things are possible. The moment we have co-current, counter current, cross current, your rate of reactions will change? Your reactor's design will change. That is why heterogeneous systems are very, very complicated. Heterogeneous rates are very, very complicated.

But the beauty in chemical engineering is whatever contacting you use, cross current, counter current or co-current, the movement of that particular phase can be visualized as either plug flow or mixed flow, that is all. That is the beauty.

That is really, my God I will get really excited when I see the reactor design because any kind of reactor you bring, you know, even from other planets also, or from our planet, we can reduce them to two continuous systems, either plug flow or mixed flow. But we have not yet decided, I mean discussed what is this plug flow and what is mixed flow yet. We will do that, right but I have to talk to, talk to you about this kinetics first so that we will have the meaning for the rate.

(Professor – student conversation starts)

Student: In heterogeneous reactions all these stages we have heat transfer and mass transfer.

Professor: Yeah

Student: Yeah. So all it is because 0:33:12.5 of physical reactions?

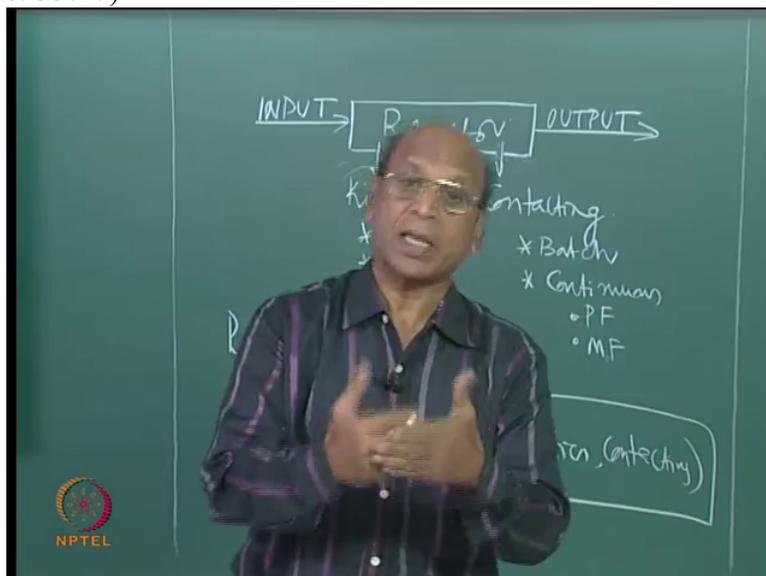
Professor: No,

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because unless these molecules come together

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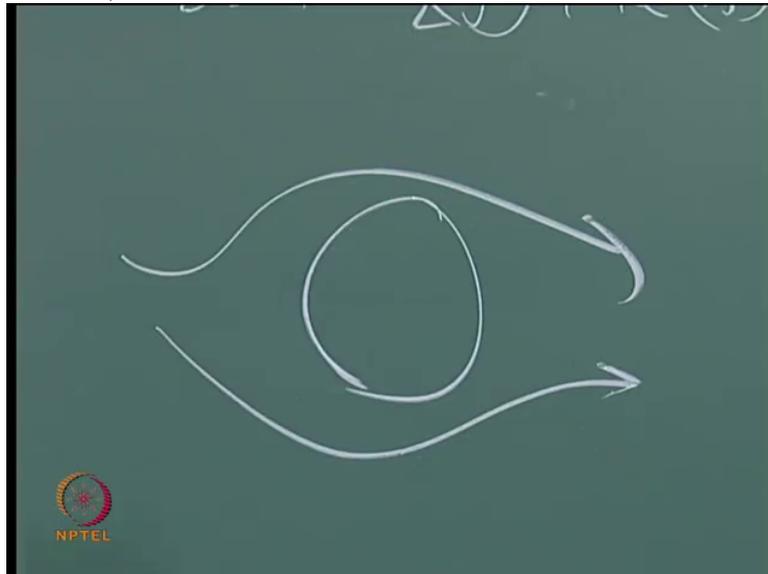
chemical reaction happens.

(Professor – student conversation ends)

But before that, Ok, now again same example. Carbon I put there and oxygen I put this side. There is no contact, right? But what is the actual condition for reaction to take place? I have to take the carbon lump, or this is the carbon, over this we are sending oxygen and fluid mechanics will tell me that whenever I have this kind of situation, no because always we draw the spherical particles, even though there are not spherical particles, right?

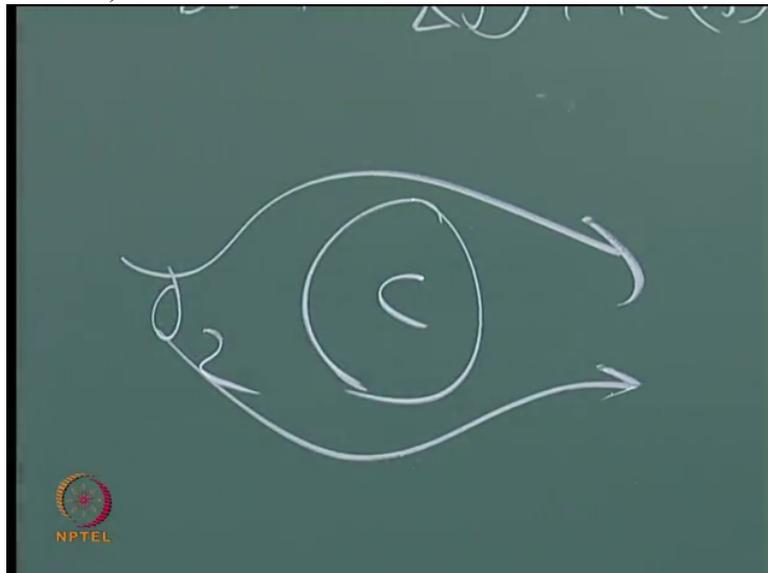
So then this goes like this,

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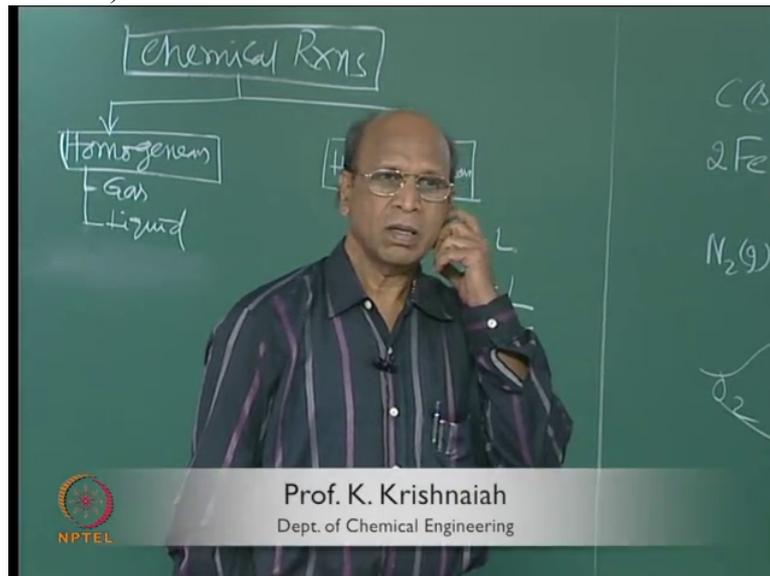
so this is oxygen, this is carbon,

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right and fluid mechanics again tells me that whenever I have a solid and gas phase or liquid phase, around this solid we have what is called, yeah, stagnant place which we call it as, which we call it as,

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(Professor – student conversation starts)

Student: Vertex

Student: Void

Professor: Where is vertex there?

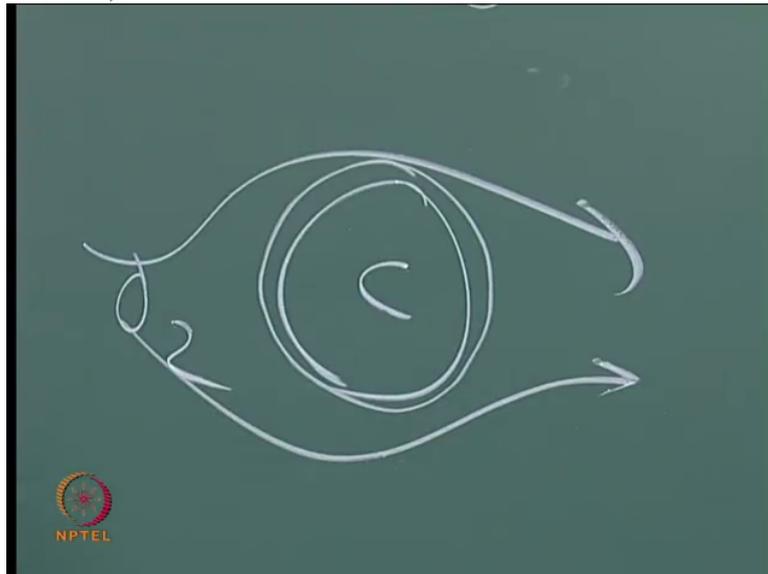
Student: Void

Professor: Not heard of? Boundary layer I say (laugh).

(Professor – student conversation ends)

Simply, you know this is the boundary. Ok that is the stagnant; I mean stagnant layer what you say,

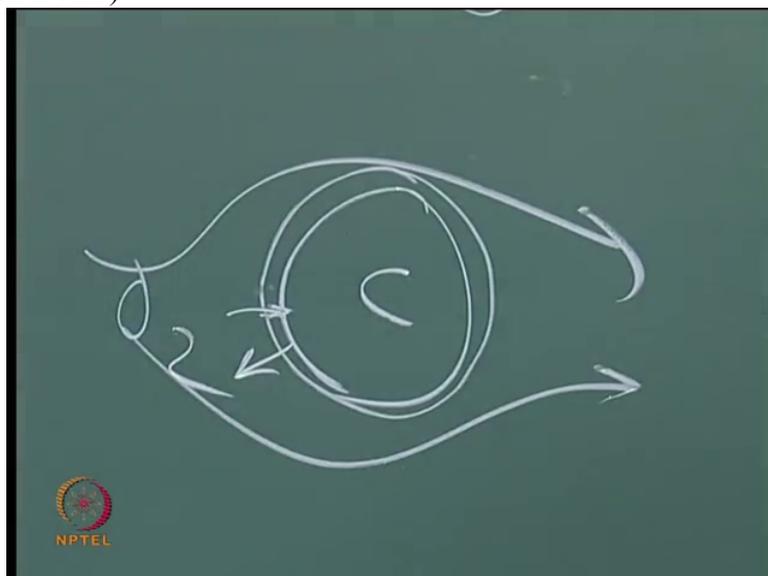
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Ok. Stagnant layer is normal word. But boundary layer is high funda word. People will get impressed when you say boundary layer. So now this boundary layer is stagnant, now you can say. Boundary layer is stagnant.

Actually that is not stagnant. It is dynamic but you know the, because the oxygen molecules are just diffusing and C O 2 molecules are, oxygen is going out, C O 2 also has to come.

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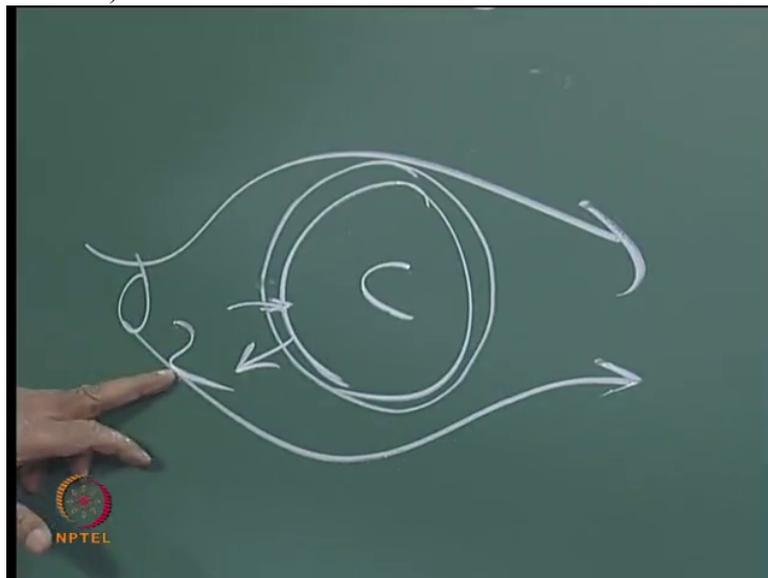
So that is why again, you know, that is why you read Fick's Law, counter-current diffusion and all that.

If correctly 1 mole is going inside and 1 mole is coming outside then you have equimolar counter and if you do not have that then you have to go for that Stefan equation, correct no, for multi-component diffusion where the mole balance is not proper and all that, Ok. So that is why that will become much more complicated. That is why we will say that Ok, let us assume only equi-molar counter diffusion.

It is only because we are lazy to do that kind of mathematical work so we will assume, we will, many assumptions we will make so that our mathematics will be simpler. But we cannot make stupid assumptions. It should be realistic assumptions where finally what your theory and what your experiment both are corresponding. That is all what we have to do.

So now this is the one. So here, yeah, oxygen...

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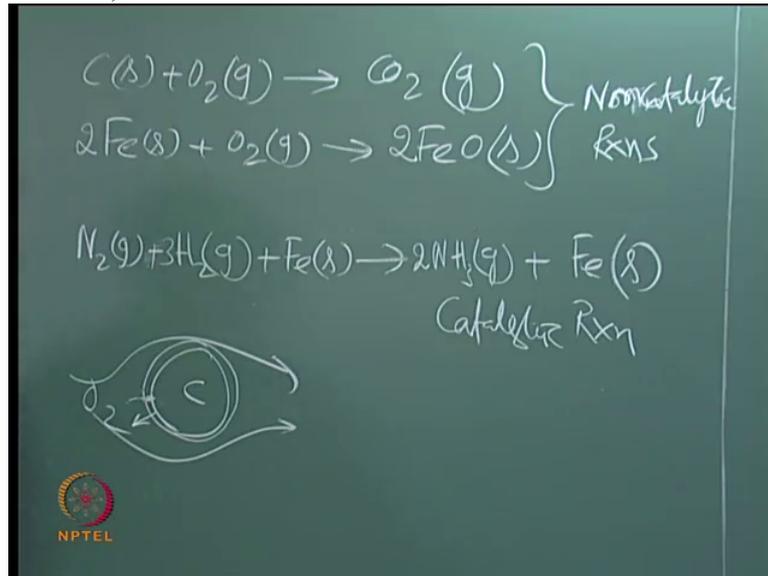


as you said, even with boundary layer if there is not much oxygen diffusion to the surface, temperature is there, will the reaction take place? You will not have. If the oxygen concentration is very, very, very low you cannot have sufficient reaction. So that is why the reaction between C and O<sub>2</sub> is a chemical reaction.

Oxygen molecule must be there and carbon should be there. Then only the reaction takes place. But what is that physical step coming? This extra mass transfer step. Not only that. If I keep, I mean, carbon we just store in the atmosphere, is it burning? It is not burning. Why? What is lacking there? Temperature. That is why heat transfer also is important.

How do you heat this particle and you send very hot oxygen or air where oxygen is there then initially it takes time for this particle to get heated up. That depends on thermal conductivity of carbon, correct no. So once it reaches sufficient temperature, then only it starts burning. That is why heat transfer is also a must step. Not only that, I think you can also take this catalytic reaction. Fe and nitrogen and hydrogen, these things

(Refer Slide Time: 37:15)



will go to the reactor at what temperature, 350 or 550?

(Professor – student conversation starts)

Student: 550

Professor: 550 degrees Centigrade. How do you bring the catalyst to 550 degrees Centigrade, right? That is heat transfer. Unless all the particles are uniformly heated around that temperature, you may not get uniform reaction rates. On the other hand, let us say that even this, yeah I have kept reaction at 550 overall, macroscopically but I will just look at one particular iron particle, Ok. What is the size they use normally? 2 to 5 meters?

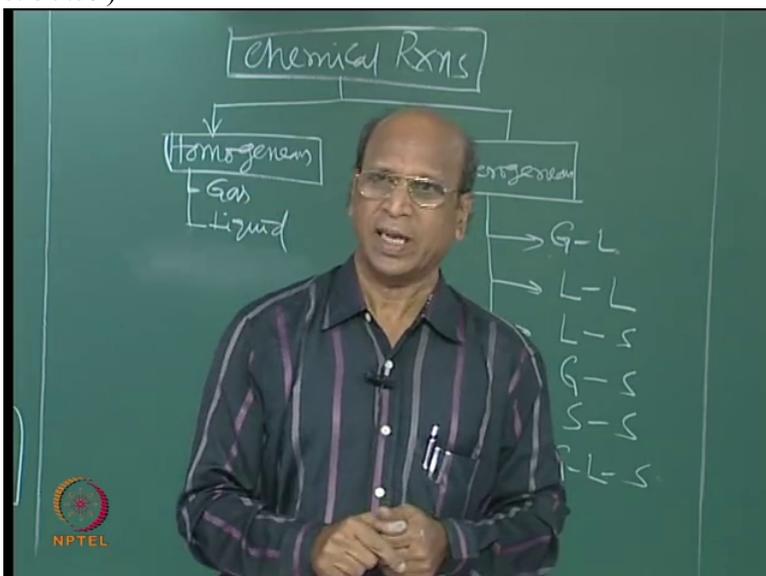
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Student: Centimeters

Professor: 2 to 5 centimeters. 2 means 1 inch,

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slightly less than 1 inch, yeah to 5, 5 means 2 inches. Any other guess? I am not saying he is right or wrong?

Student: 0:38:06.9

Professor: Yes?

Student: less than half an inch

Professor: Less than half an inch, yeah, any other guess?

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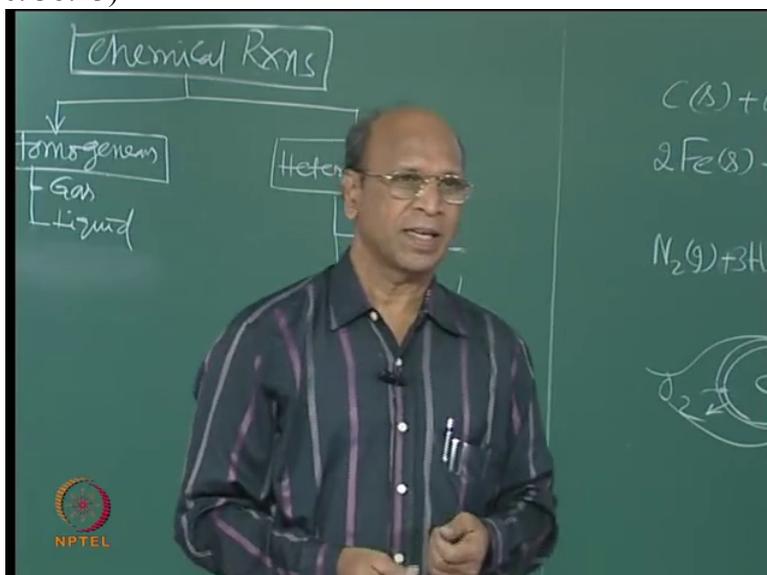
Student: powder form

Professor: Powder form, yeah. Any other, powder means how much?

Student: Microns

Professor: Because powder means, anything can be powder, right?

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Yeah, I think that is vague only, I think powder, anything can be powder. Even of course, more than 1 m m, we do not call powder. See, you know what is the talcum powder size which we apply for face?

Student: 0:38:41.2

Professor: You should tell that. Nowadays they should also tell.

Student: (laugh)

Professor: Because it is not only girls, boys also use, yeah. How much you know? Yeah, general knowledge.

Student: (laugh)

Professor: What is your name?

Student: Gopinath

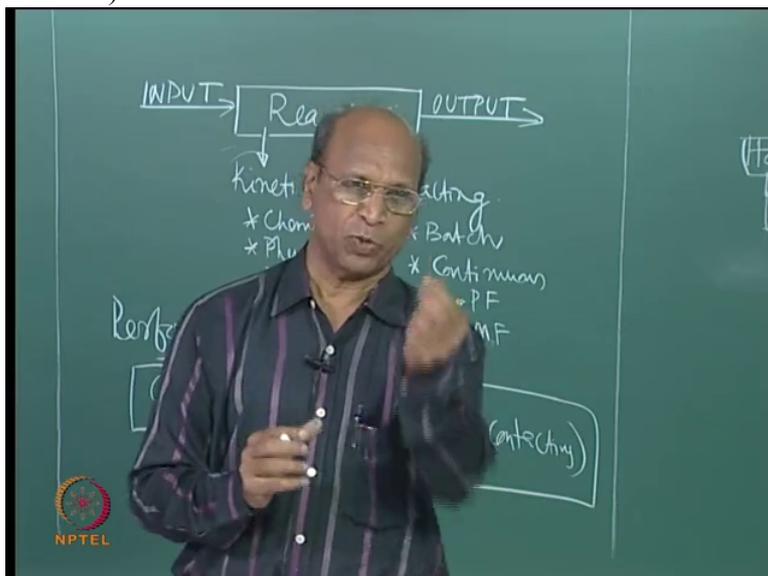
Professor: Gopinath,

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yeah, Gopinath, any guess is there? Yeah, that is also 1 micron. Just imagine that you are applying that powder with

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1 m m. Skin will come out (laugh).

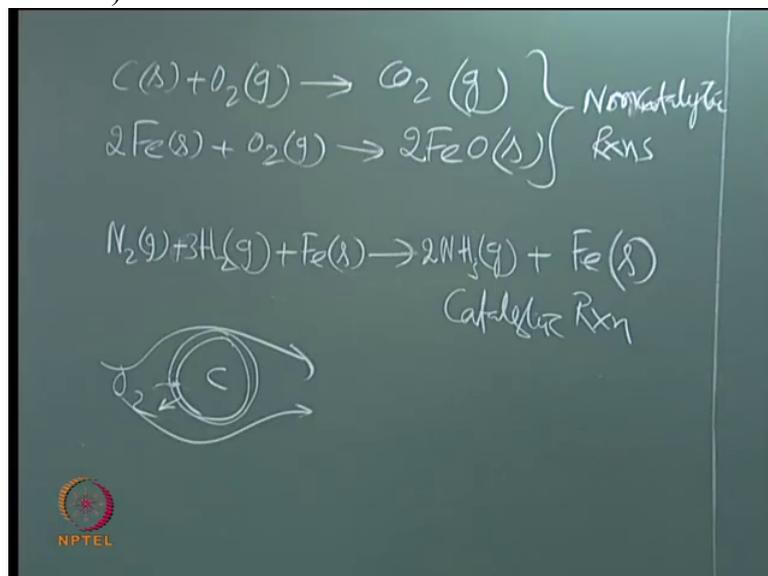
(Professor – student conversation ends)

When you are putting like this, so 1 m m that is why it is highly dangerous. You apply may be, if you are taking 5 grams and then applying here, 2 grams will go inside. Because you are not stopping your breathing and applying. You are breathing normally and then you are applying. When you put like this and then pour, something will go. That is why nanotechnology is highly dangerous technology.

Really. I know that is a silent killer. Without knowing that you are doing nanotechnology, you may be knowing that you may be doing nanotechnology but that will kill you depending on what kind of particles you are using. Those particles will happily go inside and deposit in the lungs. And everywhere throughout the body.

So if they are toxic, then that is why there is a separate research going on how to estimate the toxicity in nanotechnology. I mean we are very happy to write

(Refer Slide Time: 40:25)



no, nanotechnology and also talk about nanotechnology but these are the dangerous things, right, Ok.

So normally you know, 2 to 5, 2 centimeters to 5 centimeters no one will use. Normally it is half an inch. And particularly here, ammonia, they use, I asked you know, why they use heat

exchanger type reactor for ammonia? That is one of the questions which I asked in the first day question paper. You may not remember, I will remind it. Ok, yeah.

There is a special reason for that which also you will learn, Ok. They use heat exchanger type. Heat exchanger type means it is like heat exchanger where inside you have tubes, inside the tubes you have the packed beds. And those tubes are not normally more than 2 inches. When you have tube diameter itself for 2 inches, what should be the particle size? It may be one fourth inch. Ok

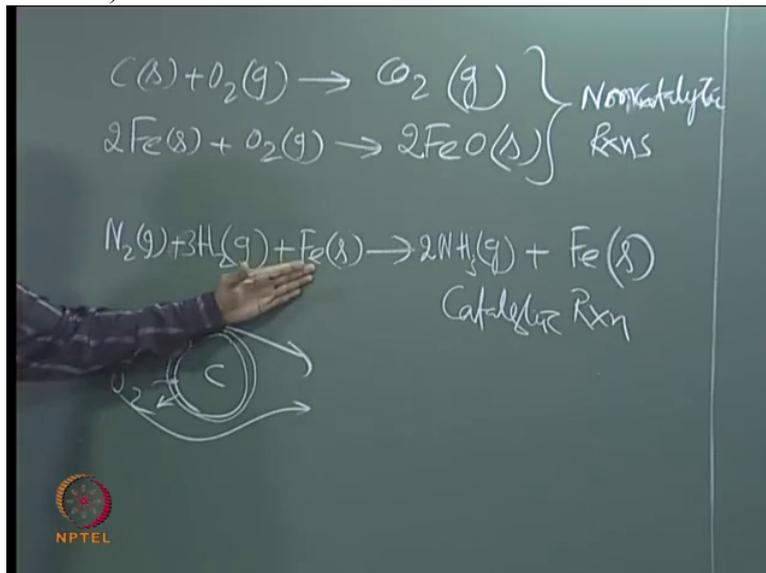
Otherwise if you again big particles, you have what are called Wall effects? You heard of Wall effects. Ok, so Wall effects means when you have large particle and small diameter, your flow will not be uniform. So that is why we say it is Wall effects and all that. That means your porosity inside that bed is not uniform.

One particle this side, another particle this side, another particle this side, and one particle is here, one particle is here, all this is vacant space. This is the diameter of the tube. So that is the reason why uniform flow will not be there.

So that is why Wall effect, minimum number of particles you should put across the, minimum across a diameter will be 8 to 10 particles, Ok, along the length, so many particles all that I will tell you when you are coming to R K D and all that. I mean these things will come there, Ok.

So all these things also we have to keep in mind when you are finally designing. So yeah, what is that I was telling? I was telling about this iron,

(Refer Slide Time: 42:10)



where packed beds, why do you use and I think you asked a question for that? Who asked about that?

(Professor – student conversation starts)

Student: p p m.

Professor: Yeah physical kinetics I think I already explained that because the physics, the two steps that, I asked you that particle because, that question because I was telling you the entire reactor is at 550 but now I will take 1 particle out. Will this particle have 550 or will it have different?

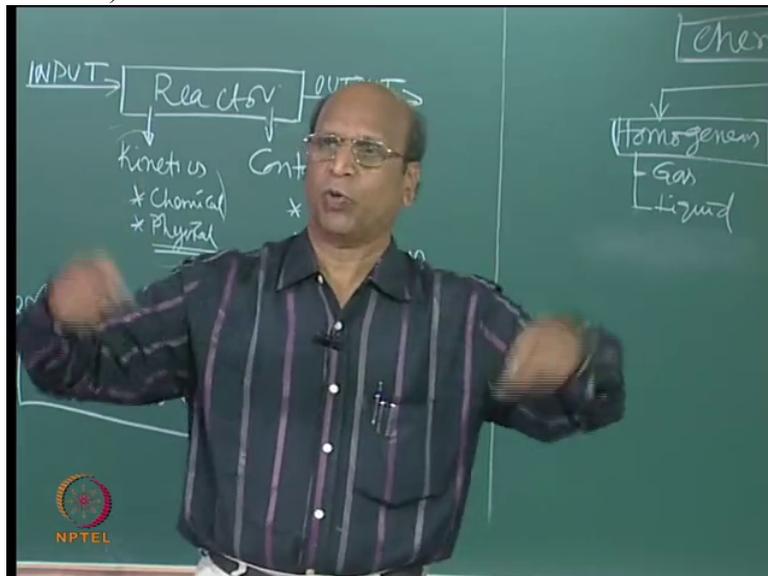
Why different, yeah you are right but why different?

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You see this is what the thinking you have to do all the time

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you know, with your mind when you are thinking about any process. It is a metal so I think conductivity is almost uniform but it is not non-uniformity of the particles. There is a very good reason. Whether it is exothermic reaction or endothermic reaction?

Student: Exothermic

Professor: Exothermic reaction, Ok. Where the reaction is taking place actually?

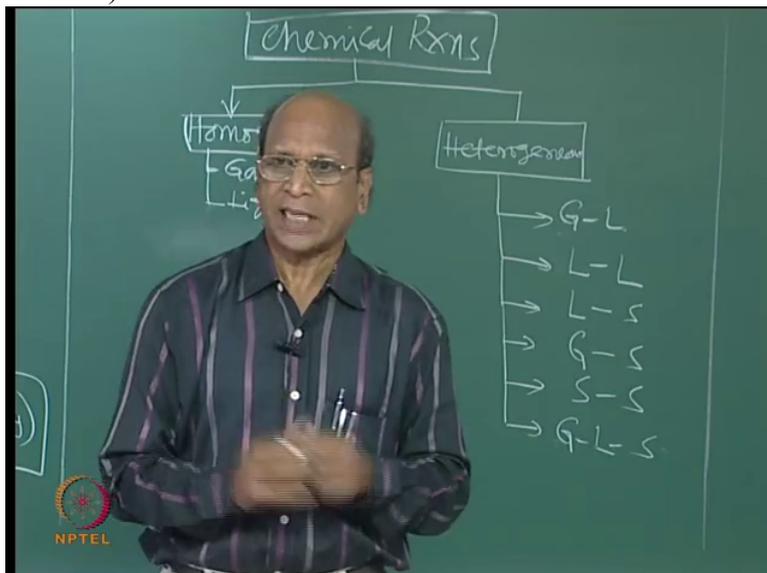
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Student: On the surface

Professor: Why surface? It is a porous iron. We can also make porous iron no? It is in fact porous iron. Because we are not

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satisfied with only external surface. External surface is very, very small. Inside the surface, you know, if I tell you, you will get really astonished. In some catalysts, even if I take one gram of catalyst can you guess what is the surface area?

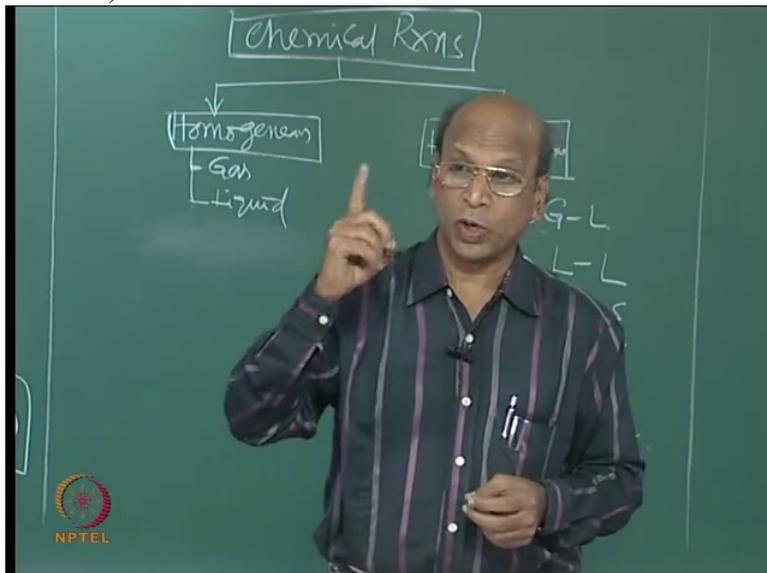
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Student: 200 meter square.

Professor: Yeah, 200 meter square, that is minimum in fact. It can go to even

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2400 meter square. in fact we produced one, my P h D student who was making activated carbon, in one sample he got 2800 or 2700 meter square per gram of activated carbon. That means you can imagine this. What is the size of football ground?

Student: 200

Professor: Olympics just now over?

Student: 2500

Student: In meters...

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Professor: Meters also you can tell.

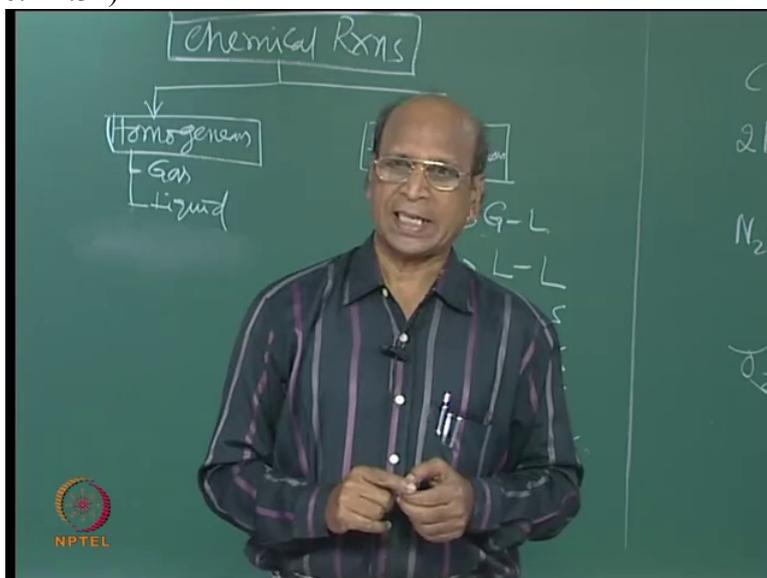
Student: 100 meters is 0:44:25.6

Professor: 100 meters and this one is?

Student: May be 25-30

Professor: More. If I remember correctly that is

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80-160 or something, 80 meters and 160 meters. Because its length is large, no, this is small.

Yeah, how much if you multiply this? Oh for easy calculation you can take no, 100 and

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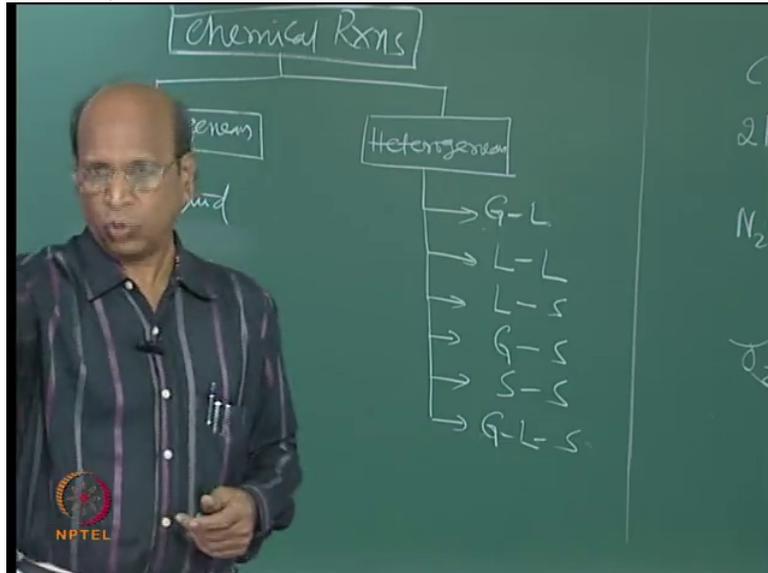
Student: 1000

Professor: 1000?

Student: 200 and

Professor: I mean 2000 you can take, right? And you know what is the catalyst per gram, of catalyst how much you can have? Good catalyst can have even 2000, 2400.

(Refer Slide Time: 45:05)



This 200 is very, very normal simple catalyst.

(Professor – student conversation ends)

And that is one of the objectives of chemical engineers, to produce as much surface area as possible. You do not have, you know, infinite opportunity to go for any area, why? Because if you are putting more and more pores, then after sometime everything will be pore, there is no solid. Ok, where is the particle?

That means mechanical strength of solid will be, that is why you have to take into mechanical strength into account and also what is the good surface area what you can get without sacrificing the mechanical strength. Why should I have, why should I worry about mechanical strength? See, so many questions I say, I can talk, talk, talk, I am not able to start C R E. This is also C R E what you are talking. Why should I worry about mechanical strength as if I do not have any...?

(Professor – student conversation starts)

Student: Catalyst will run off with...

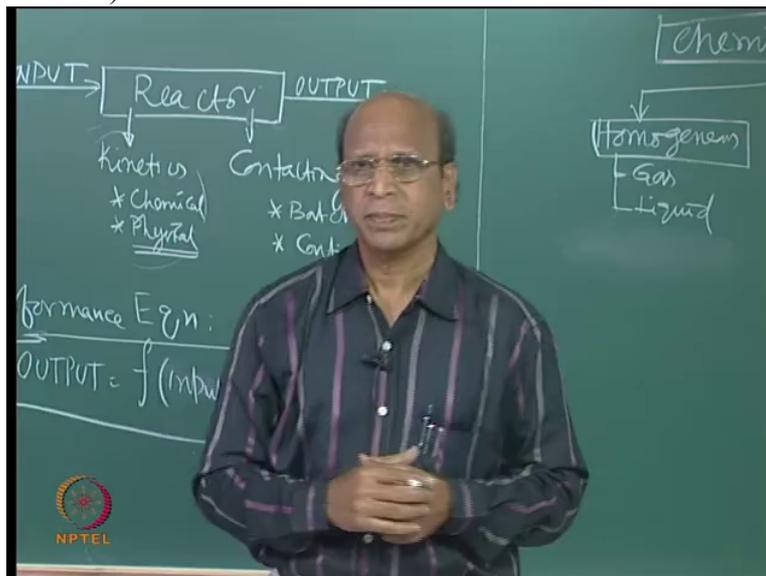
Professor: Will run off with what?

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I am taking one particle size, you know, half an inch,

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how can they run off? And also they do not run off. You put a sieve over the top of the reactor, at the bottom and also top you put, on that only packed beds all the solids are supported. You will have a perforated plate, above that, if you are not confident then you can put a sieve and over that only you will keep all these catalyst, top and bottom both places you put this. Why I should worry?

Student: 0:46:30.8

Professor: Yeah, because in industry, in one reactor you will have 2 tons, 3 tons of catalysts. And the bottom most layer should also withstand for that entire weight. It has to carry that entire weight.

(Professor – student conversation ends)

So if it is not able to carry what will happen, it will crush. When it is crushing what will happen, you will have fine powder. It is good. When it is becoming fine powder, you will get very good surface area, that is very good. But problem is that will block all the pores. Then whatever compressor you use, it is not able to push.

That is why we calculate pressure drop across the packed beds. What is the pressure drop that is required? When you have all powder, I think you or someone was telling no, powder. We cannot use powder in packed beds because of this pressure drop limitation. When you put all the powder in a packed bed, then there very, there is no porosity.

And all of them are very fine powder you take and then pack, right? Then whatever compressor you use, the gas cannot go through that. And also you are fixing that between two good distributor plates, very fine distributor plates. If the distributor plate's diameter is slightly larger than the diameter of the particle, then all the powder will come out. So all these problems are there.

That is why we take either one fourth inch, one half inch that means may be 12 m m, 10 m m, 8 m m, 6 m m that is what the particles we use. But if the diameter of the particle is, reactor is slightly bigger then normally we go for maximum 18 m m that is three fourth inch, Ok. One inch also, as far as I know, in the industry no one will go for catalyst.

Because we are losing surface area is one, but other other than that also, you know, you would like, yeah mainly it is losing the surface area, right. So that is the reason. And also as diameter of the particle is increasing we talked about mass transfer step no, the particles, the gas has to diffuse into the particle. So if you have bigger particle then the diffusion is not very fast. When you have small particle, diffusion is very fast, that means through, you have heard of effectiveness factor, effect

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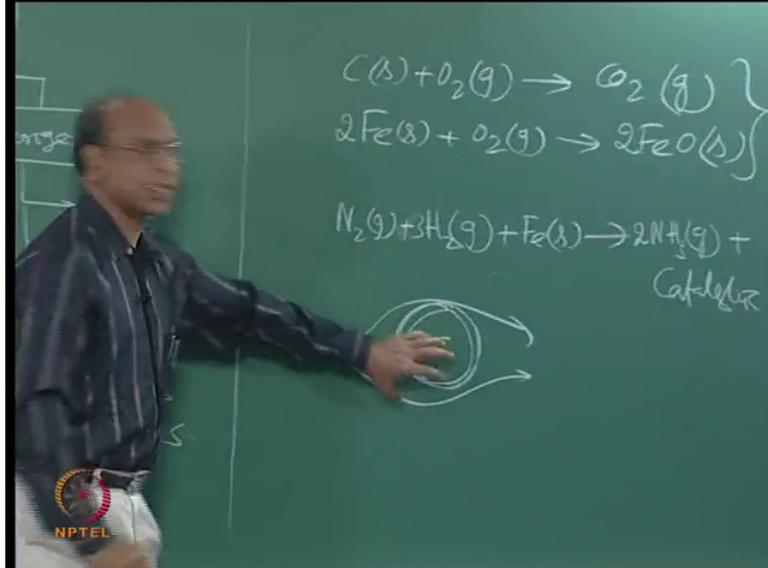


(Professor – student conversation starts)

Student: 0:48:55.3

Professor: Yeah, the diameter of, Ok if you are using this size particle,

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literally this size particle so the gas molecules have diffused from here to here, so the diffusion length is very, very large, right. Where as if I use 1 m m particle, the diffusion length is very small. So that is why it is easy for the gas to diffuse and that is why I asked the question, you have heard of effectiveness factor right? Yeah, so what does that tell you? If I say that I have effectiveness factor equal to 1, what is the meaning of that?

Student: 0:49:28.8

Professor: Yeah, but what is the condition in the particle? Right what you said is right

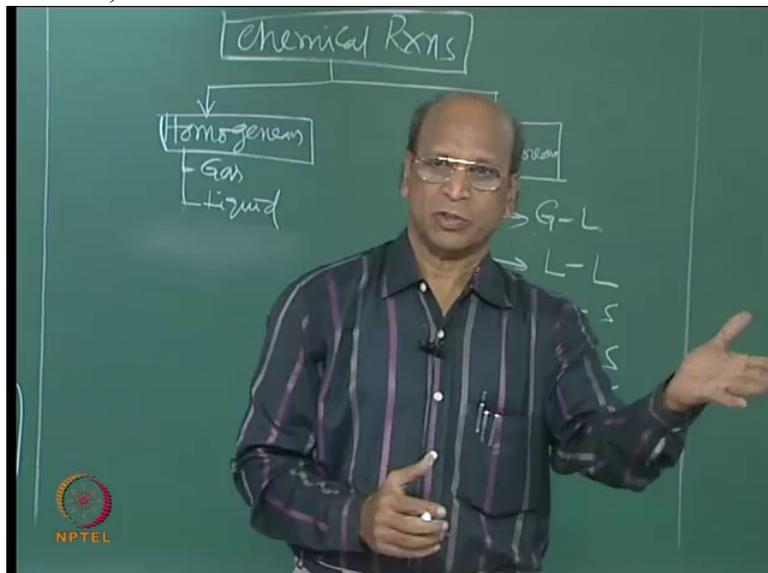
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Student: No resistance to diffusion

Professor: Yeah, so that means throughout the particle I have same concentration of bulk. That is the reason, so

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bulk concentration...practically this fellow is not allowing, I mean offering any resistance at all. That is how you have to design your catalyst. It should be porous but that pore should be sufficiently large. It should give sufficient surface area but less resistance.

(Professor – student conversation ends)

That is why, that, I know, idea of effectiveness factor, that is why you manufacture catalyst and then try to find out what is the effectiveness factor of the catalyst. So if I say that I have 50 percent only, that point 5 effectiveness factor, we are talking about isothermal, non-isothermal it will go much higher, Ok. So, because same definition. You said the rate of reaction divided by rate at bulk conditions, right?

So when I have highly exothermic reaction the rate of reaction on the numerator is very high. But because the exothermic reaction, the temperature is more only inside the particle. So when the temperature is more rate of reaction is more. So that rate of reaction and your bulk rate where the temperature is less when compared to the particle, it is small. That is why you will have effectiveness factor more than 1 in non-isothermal case. But it should only be exothermic reactions.

And in fact I can tell you in the next semester, you will get even 500, effectiveness factor even 500. That means the rate of reaction inside the particle is 500 times larger times the rate based on bulk which is very good for us. But again the problems are there. If that is so much heat is generated inside, then particle will get what is called thermal sintering, sintered.

So when sintering occurs then naturally you will not have that effective sites, active sites of the catalyst. They will die. It becomes like glass surface. If it is becoming like smooth glass surface, you know then you will not have that defects where catalytic activity is going on. That is why we say that is called thermal sintering.

And we also have the thermal deactivation. The other thing is called chemical deactivation. That means these fellows like sulphur and all that will go and then block all the active sites. And also even coal. When you burn, coke will form and that coke will completely block the surface where there is diffusion, but the actual catalytic surface is not available for oxygen to go and sit there or some other component, I mean active reactant to go and sit there. That is called chemical deactivation.

You see how many things we have to think when you are designing heterogeneous catalytic reactor. Whereas homogenous catalytic, I mean homogenous reactors, very simple. We have

the liquid A and B. You put them together, make good mixing. They are miscible, 100 percent miscible, so then A is always finding B. B is always finding...

It is very easy to get married in the U S, because A is available, B is available. One side I will love you, I will love you. Both go and then marry. Next day they may divorce, that is different Ok (laugh) but that is very easy. But here, our this procedure is very, very complicated no?

So the parents from boy's side, parents from girl's side both they have to meet. They have to high level discussions, Ok (laugh), summit discussions they call. Ok so those discussions, and now these parents will take another 5 people with them. These parents will take another 10 people with them because girls will be always more careful, you know. So that is why more people, means proportional to more number of questions. So how is the boy and all that. So that is why it takes lot of time for us. So that is mass transfer limitation (laugh)

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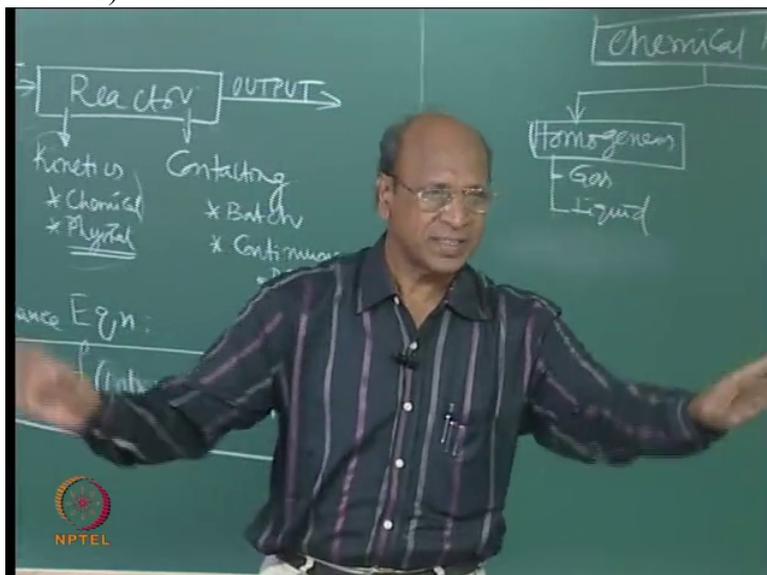


(Professor – student conversation starts)

Student: (laugh)

Professor: So reaction is not very fast. Ok (laugh), so but in the US,

(Refer Slide Time: 53:36)



no parents, direct molecules talking, yes

Student: (laugh)

Professor: Ok, happy to marry? Happy to marry. Church is open, go there, get married, come out. Next day he may divorce and all; that is different. Ok or they may stay together, no. That is why, that is what is the, you have to imagine for our molecules. That resistance only we have to remove.

(Professor – student conversation ends)

Ok, so that is why homogenous reactions, American society. Heterogeneous reactions, Indian society, Ok good. You remember that, you will never forget what is the difference between these two. What I have to do in the next class is I have to give actual definition of what is the rate, right? That means how do you define homogenous rates?

Ok, actually rate is something per unit time, correct no? Anything from some unit time, right? Your speed is also rate. So many kilometers per second. But in chemical reactions is what we do is so many moles per second reacted. That is the rate. But always we use something else there. What is that? Volume. Why do you use that? Rate is simply only that.

I would like to know only moles per time, so many moles have reacted, or vice-versa from stoichiometry you can say so many moles have been formed, Correct, no? I mean, left hand side, right hand side of the stoichiometric equation if you see, so many reacted, so many

formed. But I think always we can say in terms of reaction, you know rate of reaction, yeah, now tell me why do you use that volume there? You said volume?

(Professor – student conversation starts)

Student: How much get reacted from that.

Professor: Even without volume also I know

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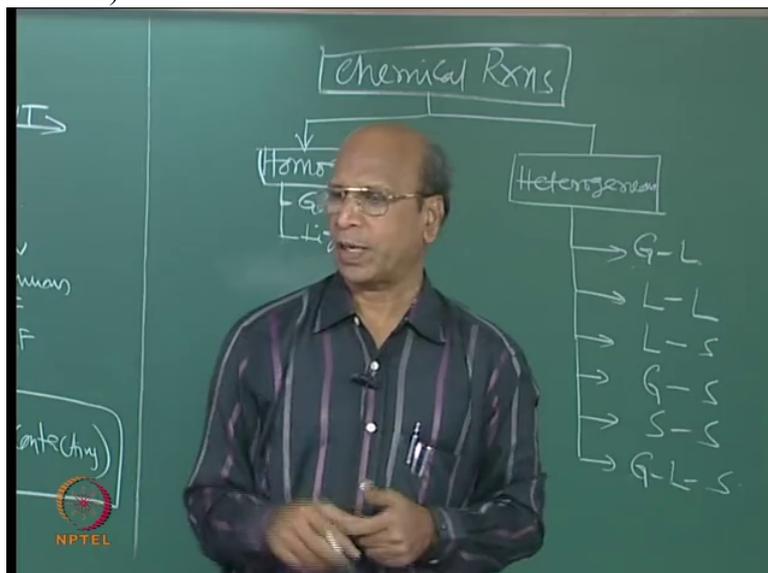
how much is the reacted, depending on the rate.

Student: Rate 0:55:28.0

Student: It can be represented in terms of concentration

Professor: Concentration is always unit per,

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I know I can take 1 liter, 1 liter that means 1 mole per liter, 1 mole per liter, but why do you use this one for expressing the rate?

(Professor – student conversation ends)

See these are all simple things; these are called cobwebs in the mind. We know rate, we know definition but if you want to discuss further we do not know. That means there are cobwebs. You know cobwebs? You can see in the house. If you clear them, then you have the clarity in the house. Similarly you have to also remove that cobwebs from our brain, then you will have clarity. That is why so many, so much discussion I do.

There is one very important reason why we do that, Ok. If I take 1 liter and 1 liter and react, my rate will be different. She takes 5 liters and 5 liters, her rate will be different, Ok, because Ok, yeah like that you know you have different people, now expressing different rates, if I take different concentrations, different volumes, then how do I simplify this? Because all of us should talk only one language.

That is why, you heard also in thermodynamics what are called extensive properties and intensive properties. What is the beauty with intensive property?

(Professor – student conversation starts)

Student: Independent

Professor: Independent of size. That is what what we want to talk here.

The rate is expressed like that, you know moles converted per unit time per unit volume then you take 10 liters, you take 5 liters, he will take point 5 liters, all of us when we convert for unit volume, we should get the same

Student: rate

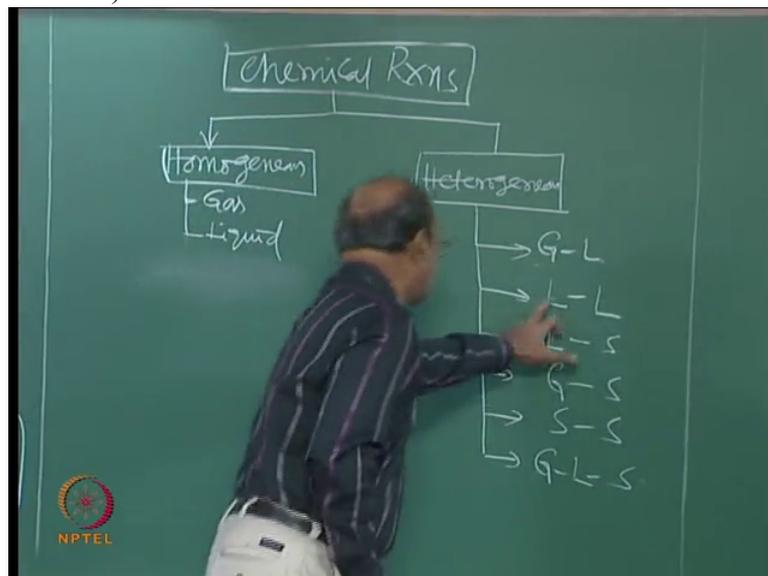
Professor: That is the reason. That is the reason why we express moles per unit time per unit volume. Otherwise I may say that Ok, my rate is 100 moles per second; he will say that my rate is only point 1 mole per second. It is same reaction, right? So, that is why the definition of rate of reaction is very important because of that reason, right?

And now the same thing if I extend for heterogeneous systems, now this volume is there. That volume is what? You know; homogenous reactions I am talking. That moles per unit time per unit volume, what is that volume?

Student: Reactor volume

Professor: Volume of that reaction mixture where both are miscible, right if it is liquid or gas and we are talking about that volume, right and now if I take this liquid-liquid,

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they are not miscible. Simplest example. So then how do I express that rate? Sorry?

Student: In terms of surface area

Professor: In terms of surface area, that is the only way?

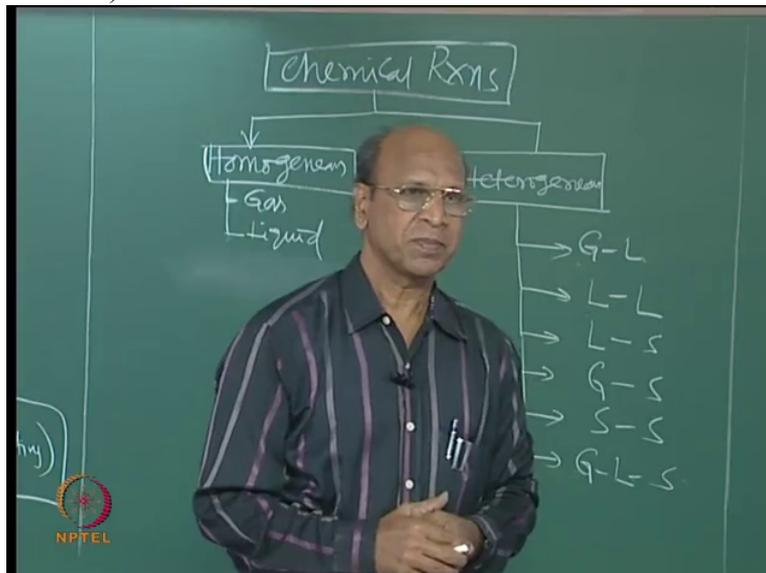
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(Professor – student conversation ends)

So that is why there are many possibilities for heterogeneous systems.

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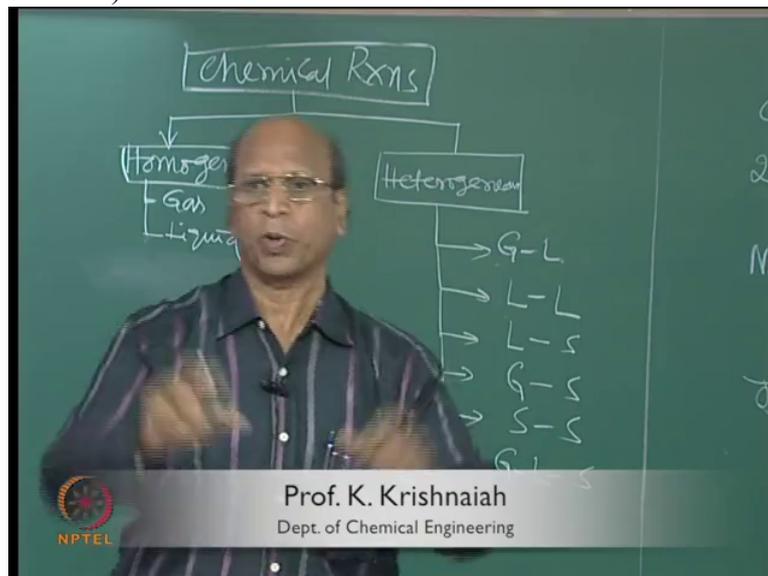
That is right, very good thing is to express based on surface area. Why? Because that is where actual reaction is taking place. But you know how difficult it is to estimate correctly the surface area, particularly in a large column where I have 2 liquids, one is called dispersed phase because you are dispersing, you cannot have two continuous phases.

Your limitation of contact is very, very low when I have two liquid, I mean two continuous phases. That is why we disperse one liquid into other who will make very, very fine droplets of one liquid into other, why? These fine droplets will give me lot of interfacial area.

That is why I told you no sometime back; chemical engineering definition is that, it is bubbles, drops and particles. If you are really able to understand the behavior of all these three, Ok and combinations then you know all chemical engineering.

So that is why what we do is, Ok it is very difficult to find out what is interfacial area, let me find out at least volume of one reactant. That we know, I am charging. Or otherwise you say, why one reactant Sir, why not two reactants? Yes, no problem.

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Or you may say why only two reactant volumes, let me take rates.

So I will say that moles converted per unit weight of the liquid, both liquids together or one liquid toge/together, may be continuous liquid, continuous phase so that is why you have many, many possibilities to define the rate. That is where the confusion starts when you are designing heterogeneous reactor. The definition itself is not clear.

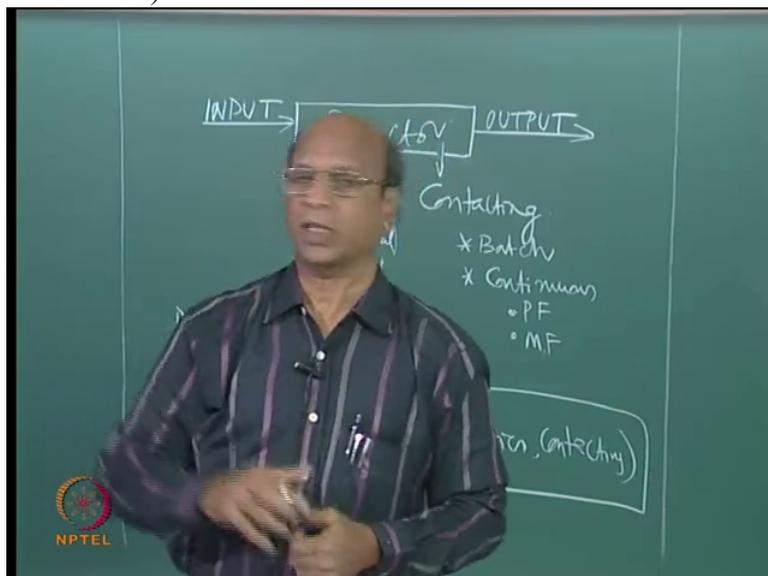
You should have seen the design of catalytic reactors, right, definitely some of you, right? So what is the rate, how do they express the rate? Rate of catalyst. Is it the only way? Need not be. You can express surface area of the catalyst. But again it is very difficult to find out the surface area. Because there are two surface areas for the catalyst.

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What are the two surface areas? One is the external and other one is all together, external plus internal together.

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Which surface area you are talking?

What you measure using B E T, B E T method no, B E T method or some mercury porosimeter what you measure is the entire surface area of the particle, inside the pores, outside surface; all together you estimate. Estimating is again difficult. That is why the simplest parameter which we can use is weight of the catalyst because I can simply put weight 10 k gs, 20 k gs, or 1 k g and then find out the rate based on weight and use the same rate so that you will get weight of the catalyst in the actual reactor.

That is why the reactor design, whatever you express, the rate of reaction on, that means you can express as volume of reactor, weight of reactor, I am sorry weight of catalyst or weight of surface area, you will get directly, in the final when you are going for this design equation, this design equation you will get that particular part.

If I use my rate based on weight of the catalyst I will get weight of the catalyst. If I use my rate based on volume of the catalyst, I will get volume of the catalyst. But this volume of the catalyst there are many, again you know misconceptions there. What volume you are talking? Volume of the catalyst means this volume has, this catalyst has inside again void volume.

Are you talking about only pure solid volume or, that means everything crushed together and you will have no pores at all, are you talking about that? Or are we talking about the volume of the particle? Or you are talking about volume of the reactor? Correct no? Reactor has now additional voidage.

Packed bed, you have the particles, this particle is porous, some void volume, so now all these particles are kept in a reactor where you have between the particles there is some more void volume. Which volume we are talking? That is why we have to clearly say, Ok moles converted per volume of the reactor, that means you are talking about the entire reactor.

Or volume of solid or volume of solid-solid that means without any voids, Ok, yeah. So like that only or volume of voids only. Volume of voids only, which voids again, reactor voids? Or particle voids? You see how much confusion is there. That is why we should have very, very clear picture of what we are talking when we are talking about heterogeneous reactors.