Chemical Reaction Engineering 2 (Heterogeneous Reactors)

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Lecture 03

Heterogeneous rate of reactions and different types of kinetic models for non-catalytic reactions

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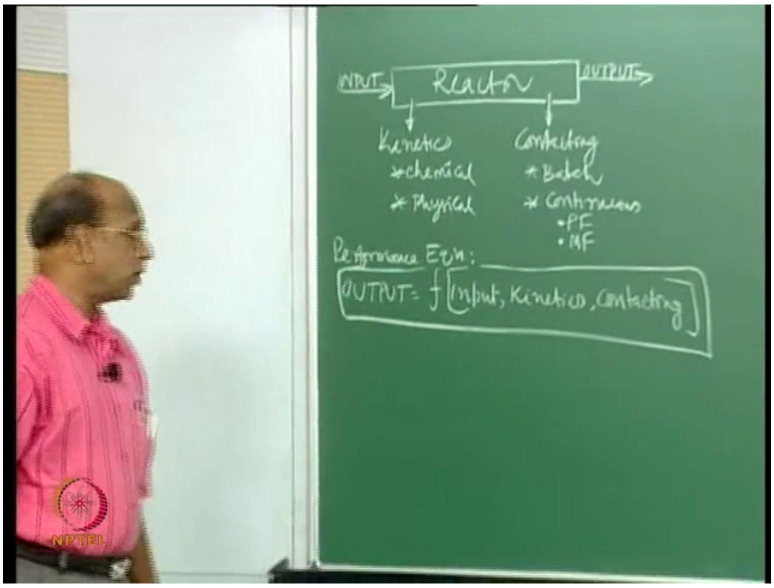

So again I have drawn this diagram to summarize what we have discussed but all that discussion was only qualitative discussion and we know that for any reactor design this is the performance equation and in this we know input that is the plant capacity you know what is the demand so you can decide what is the input to the plant and then we should know kinetics and we should know contacting.

And first we started with contacting and then found that when do you use actually batch reactors, when do you use continuous reactors and in continuous reactors when do you use plugged flow, when do you use mixed flow I hope that you have thoroughly understood. Then we decided to talk about kinetics and in kinetics you have the classification of homogeneous and heterogeneous so the method of designing for homogeneous reactors or the reactions is different or heterogeneous reactors with heterogeneous reactions is different.

And what we get extra atleast analytically with so many examples what we have decided was that the chemical factors and the physical factors both will be present in the kinetics that is in kinetic model it is not simple minus r A equal to k into C A this is a famous equation all the time in all the academic institutions because the first order reactions simplest to integrate and you know easiest to deal mathematically and also understanding wise.

So that is why always we will say that we have first order reaction and we never bother about what is mass transfer and what is heat transfer and all that but we had sufficient examples to justify that in heterogeneous systems it is the heat and mass transfer which may control the rate of reaction even though it is a chemical reaction, chemical part may not present at all that is one example which we talked about the combustion coal gas equation sorry coal combustion.

So in coal combustion many times it is the oxygen transfer to the coal which is rate controlling, okay and the rate expression will be simply minus r A equal to k into or k g into C Ag it is not k as a reaction rate constant so it is the mass transfer coefficient which you have to substitute there and then find out volume of the reactor instead of actual reaction coefficient.

So that is why always in heterogeneous systems we have chemical and physical systems both are coming and every time as I told you you will have to visualize a model write all the steps and all the steps you have to write simple equations, most of them will be mass transfer steps only one step will be reaction step and eliminate all the intermediate concentrations then you will get what is called a global rate of reaction.

Now the question to be asked which I have also told you sometime earlier during discussion was how do you define first of all your rate of reaction for heterogeneous systems? Homogeneous systems it is straight forward and always we will say that moles converted per unit time per unit volume of the reaction mixed but here you cannot have that reaction mixed because if I have a coal combustion unit I have solids plus I have the gas, so which one you really take?

So that is why there are various ways of defining the rates for heterogeneous systems. So let us also record all of them and then whatever is convenient to you as an engineer we should be able to take that, it is left to us and that is where the greatness of engineers automatically comes, you have to choose the simplest one that is possible for you for the design, right otherwise most difficult things if you take you know the design will be more complicated unnecessarily complicated, okay.

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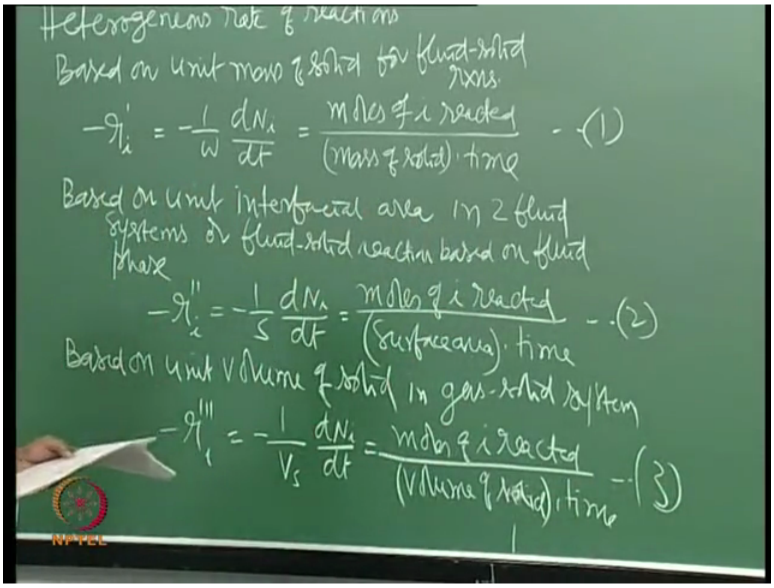

Heterogeneous rate of reactions

Based on unit mass of solid for fluid-solid rxns.

$$-r_i' = -\frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ reacted}}{(\text{mass of solid})\cdot\text{time}} \quad --(1)$$

Based on unit interfacial area in 2 fluid systems or fluid-solid reaction based on fluid phase

$$-r_i'' = -\frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ reacted}}{(\text{Surface area})\cdot\text{time}} \quad --(2)$$

Based on unit volume of solid in gas-solid system

$$-r_i''' = -\frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles of } i \text{ reacted}}{(\text{volume of solid})\cdot\text{time}} \quad --(3)$$

So based on the unit heterogeneous rates let me write here rate of reactions are defined based on based on unit mass of solid for fluid-solid reactions fluid-solid reactions you know short form of reaction is rxn like action axn, right so reaction. The overall rate or global rate for ith component in general can be written as dN i over dt and this can be also written in terms of words moles of i reacted per mass of solid per time.

So this is what we widely use if you have solid and fluid this fluid can be ofcourse either liquid or gas, right and as you know I have already told you this and weight is the easiest (()) (5:39) to measure, okay just simply weighing either 1 ton or 2 tons and then putting reactor. So but based on unit interfacial area based on unit interfacial area in 2 fluid systems that means you have gas liquid for example, right liquid liquid for example, okay.

So under those conditions or you can also say that in fluid-solid systems you can also base on the fluid not on the solid, right this is your choice but this one here this equation if I call this as one as 1 this equation is based on the solid phase I have again fluid phase there I can also base on fluid phase. So under those conditions or fluid-solid reactions based on fluid phase fluid phase how we write this one is again ofcourse to differentiate between this and this these superscripts are given 1 by S dN i by dt which is again defined as moles of i reacted per unit surface area or interfacial area and time, so this is 2.

Ya we can also base it on based on unit volume of solid in gas-solid system in gas-solid system. So that will be minus r i triple prime equal to 1 by V s dN i by dt again defined as moles of i reacted per volume of solid volume of solid ya per time, so this is equation 3.

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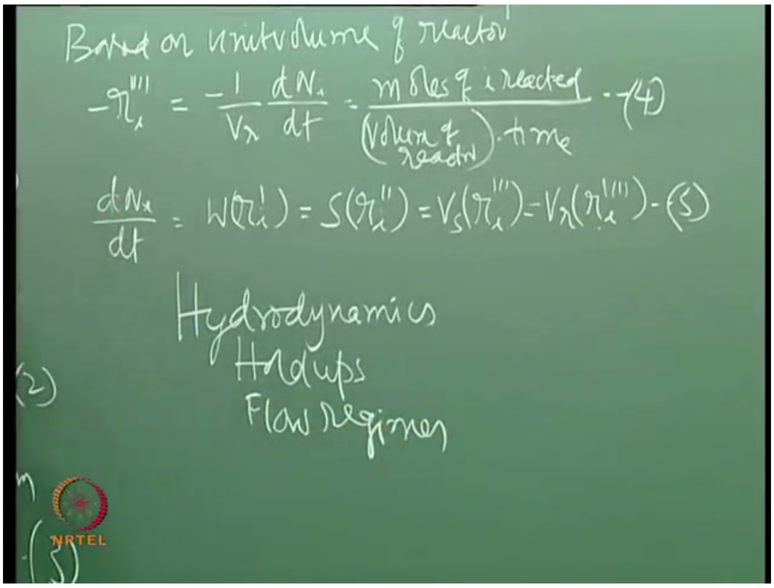
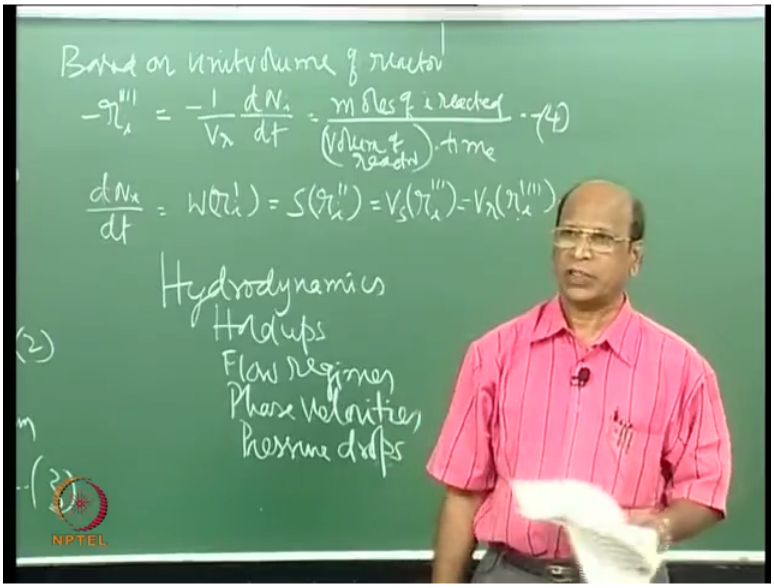


Based on unit volume of reactor

$$-r_i''' = -\frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles of i reacted}}{(\text{Volume of reactor})\cdot \text{time}} \quad -(4)$$

$$\frac{dN_i}{dt} = W(r_i') = S(r_i'') = V_s(r_i''') = V_r(r_i'''') \quad -(5)$$

Hydrodynamics
Holdups
Flow regimes



Based on unit volume of reactor

$$-r_i''' = -\frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles of i reacted}}{(\text{Volume of reactor})\cdot \text{time}} \quad -(4)$$

$$\frac{dN_i}{dt} = W(r_i') = S(r_i'') = V_s(r_i''') = V_r(r_i'''')$$

Hydrodynamics
Holdups
Flow regimes
Phase Velocities
Pressure drops

Then the last one there are many I am just giving only some 4, 5. Based on unit unit volume volume of reactor dt equal to moles of i reacted per volume of reactor per time, so this is equation number 4. In fact we can also convert one from the other these equations are simple evidence evident we can just simply write this dN a by dt is just nothing but W r i of 1 single prime then we also have S double prime, we also have V s r i triple prime and we also have V r ya so this is equation 5, good I think lot of discussion can be made on these equations how do you choose, right.

For example we say that here volume of solid and here volume of reactor, what is the difference? Karthik do you have any difference (())(10:59).

Student is answering: volume occupied by the solid particles whereas volume of reactors included the void volume in the fluid volume everything included.

Ya void volume mainly so if it is a packed bed or fluidized bed volume of reactor means it is the fluid plus solid, right or otherwise if it is only solid volume means but the true solid volume but again here there is a problem in the sense if I have a solid porosity porous particle. So now that volume also automatically taken in that solid, right so we have to be very clear now how do we define and always I prefer this one because it is easiest one but not it is true all the time.

For example if I have a slurry reactor, right if I have a slurry reactor then we have 3 phases we have gas, liquid and then solid and the general thumb rule or general convention of defining rate in a slurry reactor is moles of i converted per unit time per unit volume of bubble free slurry, okay. So what is that we have taken there it is the volume of liquid plus volume of solid because that is easiest to measure for me. In the presence of bubbles the volume will slightly rise because that much it should occupy.

So then again I should find out what is the hold up of or the fraction of gas that is there in the reactor volume that is why I think most of us will not tell you the hydrodynamics of chemical reactors. So that is much more important than actually mass transfer and heat transfer and chemical reactions because hydrodynamics they play very important role in heterogeneous reactor design we normally do not mention that hydrodynamics.

What do you mean by hydrodynamics? Hydrodynamic means we have hydrodynamics means we have how the 2 phases or 3 phases involved in heterogeneous systems they move, okay even though we call hydro but hydro general represents water right. So but inspite of that this is the general name given the hydrodynamics in chemical reactors and where you have to predict what is the fraction of each phase in the reactor volume, right that means when I am operating with certain gas, certain liquid and solids are constant for example if you take then depending on gas flow rate and liquid flow rate the reactor occupies you know certain volume of gas volume of liquid, solid is constant anyway, right.

So depending on these two flow rates how these fractions change and those are very important because if I have a reaction just imagining that I have A plus B plus C in a 3 phase reactor going to product, right. So what I told here is 1 mole, 1 mole, 1 mole but in the actual reactor because of hydrodynamic conditions gas may not be 1 mole it may be 0.01 moles because holdup is so low.

Then naturally that becomes a rate controlling step and you not have you will definitely not get more conversions, right 0.01 percent if you take you know so that is the reason why we should first know the hydrodynamic conditions in each (())(14:26) reactor not only that not only the fractions hydrodynamics will give you not only the holdups we also should have flow regimes, you know when I have two phases solid ofcourse is there as a batch system and two phases are flowing.

So if I have counter current system then it is not possible to go for very high values of liquid and very high values of gas, why flooding all counter current systems will flood, even though we know counter current system is much more efficient then co-correct system we know that but inspite of that there is a limitation on the throughput side operation side.

So that is why that flow regimes will tell me whether what should the maximum gas velocity or maximum liquid velocity which I can take this is what first you should have done in your mass transfer course also particularly for packed beds, right gas adsorption or even distillation. The first thing you do is go to that graph given in (())(15:28) and then try to read what is the maximum gas for a given liquid flow rate that automatically fixes your maximum throughputs but how do you find out this for a new column? You have to do you have to do the hydrodynamics.

So that is why all my research is not actual reactions even though I teach reaction engineering most of the time this is the first step hydrodynamics I have never come out of that even after 30 years still doing hydrodynamics on it, okay. So in every system you should be able to find out what are the flow regimes, what are the holdups and what are the phase velocities, what do you mean by what are the phase velocities?

If it is a fluidized bed, okay it may be 3 phase fluidized bed that means three phases are going solid is anyway constant the volume is a batch system then gas and liquid both we send, right but the solids have to fluidized I hope all of you know what is fluidization, right. Fluidization is the phenomena where the solid particles are kept under suspension so that they behave like fluid, okay.

So that is why we call fluidization that means imparting the properties of fluids for solid particles otherwise solids are (())(16:43) they will not move, right. So but I should know what is the minimum velocity that is required for this fluidization to take place, if I do not know that what is happening I want to use fluidized bed but most of the time it is under packing conditions packed bed conditions so that is why the phase velocities.

And the other extreme is that I may use very high velocity because I do not know anything about hydrodynamics very high gas velocity or very high liquid velocity and these velocities have already there may be more than the terminal velocities of the particles. So if you are not careful or even if you careful and then put on the top of the reactor a mesh all the particles will go that is inversely packed beds because the packing will go and stick to the top because you put a mesh they are not able to go out, if you do not put the mesh there is there will not be any particles inside the reactor at all.

So that is why that fixes the boundaries, the phase velocities that is why these are the factors normally ya apart from that the pressure drops this is also very important. So what is the total pressure drop across my column so that that is the minimum thing which I have to provide to the pump otherwise they cannot push the liquids from the bottom or from the top so the pressure drop.

So these are the general things in hydrodynamics what we have to study and all heterogeneous systems this is the (())(18:13) that is why beautifully we have a course called multi-phase systems and without multi-phase there is no chemical engineering, okay single phase systems are very very very very very few so minimum you will have 2 and why even distillation column you take, right.

So there are holdup correlations I do not know whether you have used them but the beauty of using McCabe-Thiele method is not to consider all these things it is a wonderful design I think really we have to appreciate as chemical engineers first of all I always think that how do these people get that idea that you are designing a mass transfer column without talking about any mass transfer coefficient, you do not use a single mass transfer equation, right you simply go for thermodynamic (())(19:01) draw, okay and then go for (())(19:07) energy balance which you studied in your first semester, right then balance you will get the operating lines and in between these equilibrium line and operating line chick chick chick chick that is all 10 chicks mean 10 plates, 15 chicks means 15 plates, right.

And after that we have a nice fellow called murphy and go to murphy and take murphy efficiency may be 80 percent, 60 percent, 70 percent depending on the system, okay. What do you mean by depending on the system? When do you take 50 percent, when do you take 80 percent murphy efficiency that we thought normally we tell you in the class take 50 percent you take 50 percent without questioning, okay and sometimes we take 80 percent you take only 80 percent but you never question all of you are very good students ya contacting time what do you expect in that design ya but in that method on each plate what is that we are assuming theoretically?

Equilibrium and you know what is the time required for equilibrium? Theoretically infinity, so that means you can never come back again if you go to infinity, right infinity time if you go again where are we I think we will not be there. So that is the reason why practically we have to wait for some time, right. So actually that is the rate process converted into equilibrium process but the actual rate process what we are using rate means you know mass transfer rate is the other approach we have two approaches equilibrium approach, the other one is rate approach and generally if you have a packed bed you use mass transfer equation that is why two films you draw and then you write the mass transfer equation, okay and then how the concentrations are changing, how the mass transfer coefficient at each degree height along the column all that you integrate and then you ofcourse again as an engineer you will again simplify that in terms of N 2 u, H 2 u and all that because easy to convert for the design.

So these two approaches but there also you need the this phase holdups, you need flow regimes, you need phase velocities and definitely you need pressure drop, right and pressure drop luckily we have only one equation for packed beds we have to thank (())(21:33) and story is that I do not know really we have to believe this or not someone was telling me that story some not Cambridge university some university from UK it seems when he submitted his thesis on the pressure drop of you know pressure drop packed beds he was failed because there was no contribution from him you know for P.hd you know some contributions some totally new knowledge which has not been existing till then, right.

But I think people thought examiners thought at that time that you know there is no sufficient newness in this pressure drop of the fluids through the packed beds he was failed in the examination but you know failure only we have been now using even after 70, 60 years that is only equation what else you have? All other equations are only some extension delta x, delta x extension of that same equation the same thing even at Monod’s equation or Michaelis

Menten equation one of those I do not remember now one of those papers have been rejected saying that this paper is not work publishing.

You see in the history of this research and then you know development of concepts some things which we have thrown out that it is useless concept later than the only concept that was valid, okay. So all beautiful histories are there if you just try to understand how chemical engineering developed or any process developed, good. So hydrodynamics are very very important for heterogeneous systems, good.

So and most of the time if you look at the rate at the equations given in the text books if it is a packed bed many times this is the one that is used, if it is a slurry reactor many times that is used is based on volume of ya bubble free slurry that is what and if it is gas liquid system you do not have any choice except that you have to go for interfacial area. And you see the most difficult thing in chemical engineering is finding out interfacial area or surface area.

For solids it is fine solids also have interfacial area but I can easily find out solids, interfacial area if I know the particle size even particle size distribution. So I will go to (())(23:50) which you learnt in your maybe 4th semester 5th semester mechanical operations and then you have various (())(23:57) may be between these (())(23:58) each time you will have may be 10 percent, 20 percent, 40 percent like that and in each category within that you know what is the particle size average size find out that interfacial area surface area so like that all surface areas we can add up I am talking about just external surface area (())(24:15) gives you only external surface area because what I am trying to say is particles are not changing with time even in the packed bed so you can easily find out what is the interfacial area based on external surface area alone.

But you also have fairly very good techniques to find out what is the internal surface area for the porous particles. Now what are the methods? BAT is one method and you also have mercury porous emitters but BAT will give you to certain range of pores and mercury also mercury porous will also give you certain other range of pores but all these pores we have add and then find out what is the total surface area and that will be very useful for catalytic reactions but advantage there is those particles are not changing with time unless you have a deactivation, okay.

So that is why I am very fairly confident about that but the systems with gas liquid and also liquid liquid very difficult because you have in the liquid liquid system droplets one is continuous phase, other one is the dispersed phase in the dispersed phase we have the small bubbles, large bubbles and unfortunately large bubbles will become will break and then become small bubbles and small bubbles will (())(25:32) and then become large bubbles we do not know how to really predict what is happening throughout the system in the process, that is why that is one of the most difficult parts in evaluation in evaluating the interfacial area and much versus your bubbles also, right.

That is why if you are able to design a system where you can beautifully produce only single bubbles or single droplets of uniform size then this very very accurate surface area is very very accurate because I have only I have to measure only one bubble size, all bubbles are same after words. So then simply multiply by number of bubbles and then each bubble what is the surface area that is why I like this screensaver whether is one screensaver with bubbles I think in windows 7 also.

So I mean I always put that wherever I go I have computer in house or computer here wherever I see I have that possibility I will push that screensaver because thinking that how beautiful it would be if I am able to produce that kind of highly beautiful spherical particles on the screen, okay. But same thing if I can extend to my research area also that will be wonderful and I am doing some work on the inverse fluidized bed (())(26:49) maybe 10, 12 years.

So there we have observed this kind of uniform bubbles, okay inverse fluidized bed is used for waste water treatment, the liquid is sent from the top because these are the lighter particles that is why it is called inverse fluidized bed, the particles if you just put in batch of liquid this will flow to the top because they are lighter particles lighter than water. So now to fluidize that I have to push from the top, right and that pushing liquid is in simple terms it is the waste water, right and then this is a biological process where the microorganisms require oxygen.

So that is why I now send my air from the bottom, okay it is 3 phases counter current system. And why should I use an inverse fluidized bed why cannot we use a normal fluidized bed this can be used. The advantage of inverse fluidized bed is the particles are lighter particles so they have less inertia less inertia. So due to this less inertia the particles can easily move, okay or rotate. When they are rotating they will destroy the film liquid film surrounding the particle, what will happen now? Ya mass transfer ya fresh area generates and then mass transfer is maximum.

So when mass transfer is maximum and particularly if mass transfer is controlled and for even biological processes mass transfer may be controlled oxygen supply for example that is why I told you already waste water treatment open ponds, right very big large scale very very large area you have to use the reason is that you do not have an efficient way of mass transfer to each and every microorganisms so they do not work they will die of suffocation.

So that is why you have to use large size to compensate for your final production rate. So in this inverse fluidized bed it is not, right because it is very efficient system where this will break in fact it was found that may be 1.5 to 2.5 times the mass transfer coefficient can increase and number wise you may think it is very small. So that means it is directly proportional and mass transfer coefficient doubles means area will be half area of the system what you are using.

So that way it is very advantageous there what we have observed was when the bubbles are coming and the particles are expanding down, right and in between those particles the bubble size is almost uniform because the gas has to go through the bubbles I mean through the particles and the liquid is trying to expand the particles. So depending on the density holdup of the solids if the holdup of solids is more almost like a packed bed I guarantee almost uniform bubbles throughout and definitely I know that how much mass transfer you know oxygen going to be liquid, then that liquid goes to the surface of solid on the surface we have the microorganisms.

So microorganisms happily take the nutrients or the food from the waste water and also (()) (29:58) the dissolved oxygen then happily it will work, it will reproduce because good enrolment for it because it is a good food and good oxygen amount of oxygen. So that is why what is the next one that is left in the nature? Reproduction, so that is why more and more microorganisms also are developed or produced then you will have very efficient process, there also we are studying all the term even now we do not have correct equations for minimum fluidization velocity for example this space velocities, we do not have an equation for pressure drop, only recently we have a developed that.

And I think I have to publish that I think we are the first people to say to give a pressure drop equation till now in the world that not yet published only student recently submitted these thesis, there is no equation for pressure drop in a inverse fluidized bed. And ofcourse the flow regimes, flow regimes we have not yet done but there are just only one or two papers for studying flow regimes.

And ofcourse holdups many people study and beauty there is if I do my experiments it is not tallying with other experiments. So we have some 6, 7 others we have published this holdups everyone has the different correlation, I do not know what to normalize now in fact my next item is that you know what is that why different people are given different correlations I am telling all this even in this course because that is what the information you need if you design a new system it is not existing then you have to develop all this holdup correlations, flow regime map and also phase velocities, pressure drop correlations all that otherwise you cannot design the equation I mean you cannot design the reactor, right okay.

So this is what is the what the are general difficulties when you go for kinetics and we decided now we have to concentrate or throughout this semester we will talk most of the time on the kinetics part of heterogeneous systems and the first one what we take in this is gas solids non-catalytic reactions, okay then we will take gas solid catalytic reactions, then we take the fluidized bed fluidized beds will come under gas solid catalytic reactions, then we will take slurry reactor, right.

So in gas solid non-catalytic reactors we will try to design packed beds and also fluidized beds and in catalytic reactions also packed beds and fluidized beds and in slurry reactor ofcourse there is only one slurry reactor, right. So this is the overall picture first finding out the kinetics that means kinetics models have to be developed and then we have to use that information in the design of the reactor for either packed bed, or fluidized bed, or moving bed, or rotary kilns procedure is same but we cannot do everything in this course so atleast this important things and very frequently used reactors are this packed beds, fluidized beds, slurry reactors in the industry. Moving beds also are used but I think very difficult to control moving beds, rotary kilns are again very easy and the design also very easy I think even though we do not have to design that but it is very easy to design I will let you know when the time comes and rotary kilns are mainly used for gas solid non-catalytic reactions ofcourse ya solid solid reactions and non-catalytic reactions like gasification, okay so people use the rotating kilns, okay good.

So that is the overall picture and now we will go to gas solid non-catalytic reactions and first to know in gas solid non-catalytic reaction is what kind of reaction first of all you gave you may be wondering what do you mean by what kind of reactions, okay. So example I can say simply tell you if I have iron ore reduction Fe_2O_3 plus H_2 giving me Fe plus H_2O, okay ya that reaction is quite different that is also non-catalytic reaction gas solid when I compared that with gasification reaction or combustion reaction what is happening is here coal plus C plus O2 giving me CO2 but there I have this solid product at the end in iron ore reduction, whereas here I do not have anything because particle will disappear you may have ash and there are coals where ash is almost negligible 5 percent ash, 10 percent ash.

So then there is nothing in the reactor then how do you design the reactor you do not need any reactor which means. So that is why and also there are some beautiful reactions non-catalytic reaction for example you are using our computers and all that very happily, right and silica is one of the things which chips to make and you know how difficult it is to produce that pure form of silica and once reaction that is used is Silane that also I will write SiH4 going to Si plus 2H2.

So that means actually it is a gas and after reaction I see the solid product, wonderful design and I guarantee you if you develop a process now there are many companies that are trying to do in the world you will become a millionaire why millionaire you can become a billionaire, if you are able to develop that process of producing pure silica, in India no one is producing we are only importing and ofcourse one good thing with us is we do not design chips, okay.

So that is why you do not have to import that much silica someone else is doing that. So that is why very big companies like union carbide now union carbide ofcourse is joined with some (())(35:52) ya those people are still trying to get the maximum there are some processes but which are very costly which are difficult, not only costly process wise difficult that means slight change in the process conditions we do not get silica.

So how do you design your robust process and then try to get the purest form of silica there are still many many reactions like that and another wonderful non-catalytic reaction I can tell you is ceramics, Chinese have made this technique long time back beautiful you know Chinese porcelain is one of the wonderful qualities, right but we do not have that kind of quality that they are doing even now by art rather than using science because the solid solid reaction is also not that easy to understand and then try to use the scientific information for the design of Tea Cups or Coffee Cups, right.

But you see the greatness in the art because art has been developed over the hundreds of thousands of years that is why they became experts but unfortunate thing is only that family is expert in that they cannot communicate with anyone else but if I have a scientific method whoever understand science happily they can use that information that is the difference between art and science because suddenly I cannot become a painter, only it is possible for M.F Hussain may be after words his children I do not know anyone is his children really painting or not because genes will definitely work to some extent, okay all of us know that doctors becoming doctors, tennis players becoming tennis players you know the family cricket players and maximum number you can say that movie actors becoming movie actors that is maximum fraction.

So these are all always a little bit genes and then enrolment, right because from morning to evening in movie actors house always they discuss about movie that is good, this is bad, I fought with 100 people, I fought with 10 people today on the screen. So all that they will be discussing so slowly the genes also try to change you know through the enrolment saying that okay finally I have to also become like that, right so that is why this first identifying what kind of reactions we have is very important, right.

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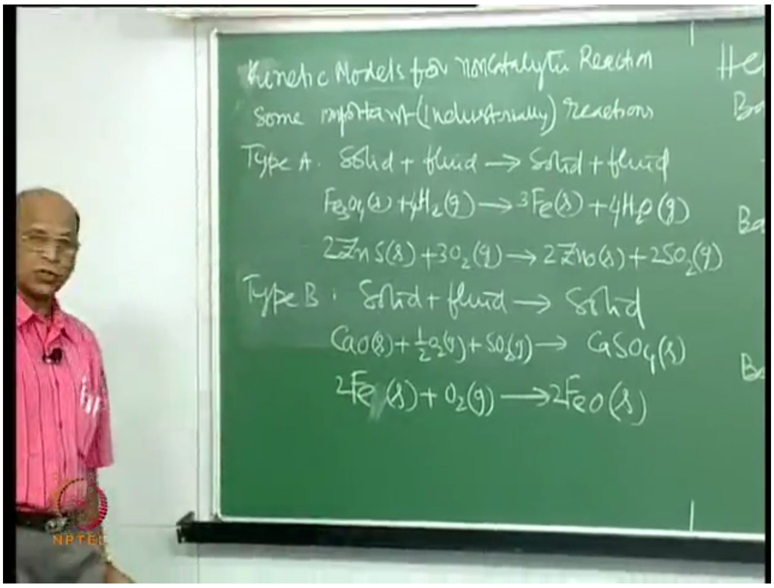

Kinetic Models for noncatalytic Reaction

Some important (industrially) reactions

Type A. Solid + fluid → Solid + fluid

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

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

Type B : Solid + fluid → Solid

$CaO(s) + \frac{1}{2}O_2(g) + SO_2(g) \rightarrow CaSO_4(s)$

$2Fe(s) + O_2(g) \rightarrow 2FeO(s)$

So now that is let us just list out some industrially important reactions. First I have to take (non-catalytic) okay kinetic models for non-catalytic for non-catalytic reactions. So let us say some important important okay I can write industrially reactions, okay we will divide this into different types and I will say that first I have type A reactions where we have solid plus fluid going to again solid plus fluid I think just now I have told you one example, what is that?

Ya so this is Fe3O4 solid plus H 2 gas giving me Fe solid plus H 2 O gas, okay so I have to balance this 3 so then this is 4 ya then this is 4 ya that is one reaction. The other reaction is ofcourse roasting of zinc zinc ore ZnS solid plus O 2 gas giving me Zn O solid plus SO 2 gas so again if I balance this is 2, this is 2, this is 2, this is 3 I think (())(40:42) 2, 4, 6 ya okay so that is the reaction there are many but I just want to give you only one or two so that you are comfortable this is type A.

And type B we have solid plus fluid giving me solid I have my favourite reaction here that is calcium oxide Cao solid plus half O 2 gas plus SO 2 gas giving me Ca calcium sulphate and this is one of the famous equations for removing sulphur from flue gases, you know thermal power plants and all that you have. So from there using this reaction you know sending this amount of oxygen, this amount of if you have this amount of SO 2, this amount of Cao you can always this is what one of the very one of the methods very widely used in fluidized bed combustion, you know in fluidized bed combustion what do they do?

Fluidized bed combustion is very famous particularly for sulphur coals and high ash coals, okay fluidized bed combustion, okay and it is a fluidized bed where along with coal they also put calcium carbonate particles calcium carbonate is nothing but our Taj Mahal, okay ya they do not put Taj Mahal I think you know calcium carbonate particles they just put. What happens is this calcination step is the first one calcium carbonate is CaCo3 and if you expose that to very high temperatures then you will have Cao plus C O 2 that is instantaneous reaction that is why you simply through calcium carbonate particles in the fluidized bed chamber then first reaction is instantaneous it becomes Cao at any time I will see Cao.

So now this another example for me to tell you rate controlling step, which one is the rate controlling step? Either this one or the first one where calcination CaCo3 becoming to Cao this one is the rate controlling step because that is instantaneous that means any time I see that I have calcium oxide that means because calcium carbonate has been converted to calcium oxide, right.

So then this reaction takes place and you know there are many beautiful things about this there are atleast may be 100 papers on this, how this reaction is taking place with Cao, okay. So what is the beauty in these reactions is that this one this calcium sulphate has more molar volume than calcium oxide, molar volume. So that means the volume of particle will increase during the reaction and that is bad for the reaction because the calcium carbonate when it is becoming calcium oxide you have lot of pores, lot of pores means like our (blood) like our bread you know what you take, okay more pluffy the bread is the more porosity in the bread just imagine you know without porosity you are trying to eat bread that becomes roti, okay ya it is not bread.

So that is why this greatness of this modern bread and all that to make lot of porosity but still you know it is nicely eatable, right. So that is why immediately that it forms pores inside the particle then (calcium) sorry then SO 2 will try to diffuse into that.

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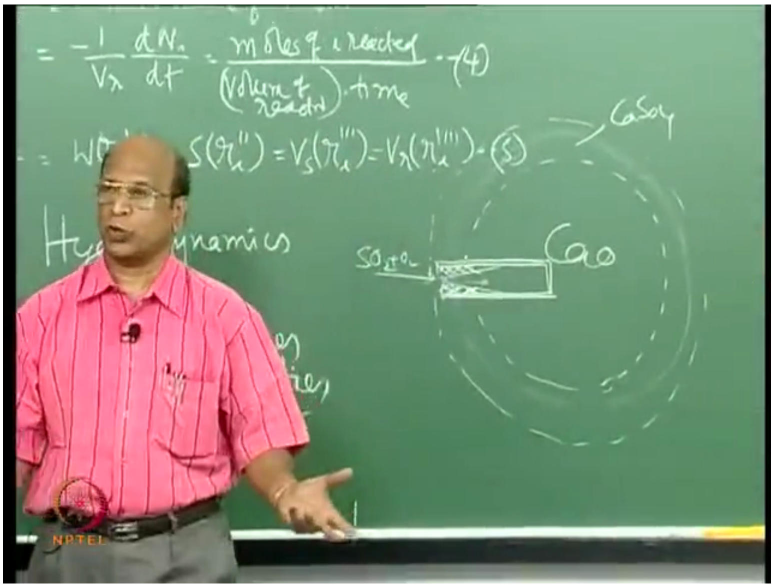

So if I just look at one pore this pore may be something like this okay one pore just one pore and I have some thickness of this pore and SO 2 is trying to diffuse there this is SO 2 ofcourse with O 2 and all that, right.

So then what happens because here I have more (concen) diffusion know by diffusion if I draw the profile the concentration SO 2, O 2 profile will decrease because of the resistance very small pores. So naturally that decrease in concentration will come and you have the maximum concentration at the mouth therefore rate of reaction is more faster. So when the rate of reaction is more here calcium sulphate ya forming will be more and that forms something like this, this is the calcium sulphate you see now this pore actually now this is the mouth of the pore, all this is solid.

So after sometime what happens is this SO 2 or O 2 cannot go inside these blocks but still I have large amount of calcium oxide that is left inside this, this all waste that means if I visualize one single particle, if this is the particle size where the reaction is practically taking place ya only this one that is where you have calcium sulphate and all this is waste water that means I am generating now lot of solid wastes or not good quality of calcium sulphate because outside calcium sulphate inside actually I have calcium oxide that is why in Germany I saw one company Luggi ya what they do is they spray water on that after sometime of reaction they spray water on that I mean you can also do not only in combustion you can do this even outside you know flue gases can be taken out first and then have the calcium same reaction in the separate reactor that also they can do.

So there they spray water, what do you think will happen if they spray water? Ya because you know the solubility of calcium sulphate that is very high in water but it will just absorb water and then that water will go and touch the calcium oxide this is Cao and you know the reaction between Cao and water what kind of reaction exothermic or endothermic but is it exothermic reaction or endothermic reaction? Highly exothermic reaction I do not know most of you would have not put this white wash in your house you try to buy calcium hydroxide you know calcium oxide and then make as calcium hydroxide and then try to bubbles actually, it seems that is one of the punishments that is given to in olden days one of the punishment that is given to I mean thieves and or murderers by Kings you know what they do?

They will ask the person to stay like this put all calcium oxide around them and put water all his bones becomes calcium it is just you know life burn really I mean it was recorded in some ofcourse ruthless people at that time Kings normally we need them now otherwise things may not work here in our Country, okay. So that is why that exothermic heat is used to burn the body, right.

So what happens is when so much heat is generated inside and the remaining some of the amount of water which is going that evaporates. So when it evaporates it has to come out, what does that do? It breaks and come out, so when it breaks and comes out all this area is again inside exposed to calcium oxide I mean for SO 2 and O 2 for reaction to take place. You see these are very beautiful simple technique which we will never normally appreciate that is why tremendous amount of good innovations are in industry but they never record because by recording if someone steals like that movie Inception or other things, okay.

So then they will make millions other people also make millions this company will go that is why everything is kept under a secret but tremendous technology. In fact this Silane Si from Silane is one of the really strongly gotted secrets by the industries because you know without computers and evidence we cannot leave, right that has become food for us 2 or 3 days if you do not have computer I mean we do not have food it is okay but one day if you do not see your emails entire world will come out. So there are otherwise if you do not tweet tweet you cannot sleep, okay or if you do not chat with your friends whatever you eat also it will not get digested.

So that is why so many things are there you know with computers so the demand for silica is maximum, right. So I think someone who is interested in technology can always go for this production of silica pure silica as chemical engineers. If one of you can do that I think it is excellent you will become billionaire and then you can come to IIT as Chairman Board of Governors, okay ya that is what normally you know very high level industrialist or academicians are given as Chairman Board of Governors to Directors what we have to do in IIT's okay anyway.

So this is the information about the ya okay type 2 the difference between type A and type 2 reactions and this is one of the famous reactions and another there are many for example rusting of iron that every day we see but we never appreciate that one as one of the non-catalytic reactions, right okay.

So this is Feo solid plus O 2 gas giving us Feo Feo solid again you know this is I mean for we everything is exiting I say I do not know for you how many things are really exiting. Now every day we see here and the rust also in what form that nicely all the time. Sometimes if you see your cycle you will see that you know some material will come up as flakes and somewhere it will beautifully deposit as grains oil you never discuss, you never even observed ya that is what that is a chemical reaction, okay that is what my interest is different form of corrosion is not simply it is non-catalytic reaction but ofcourse it is matter of what is happening obvious any cycle whatever is buy is it stolen, right I think in (())(51:48) many cycles are stolen that is what people are telling, okay ya this is balance 2 know, this is 2, this is 2 correct ya. So like that we can list out even type A, type B then there are two more or three more.