Advanced Chemical Reaction Engineering
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Lecture - 30
Gas Solid Reactions Temperature Effects on Rate & Equilibria
Introduction to Population Balance –I

We are going to be looking at gas solid reactions effective equilibria. Now just to give you a background on this whole effect of equilubria, let us just look at what we have learnt in our school on the blast furnace.

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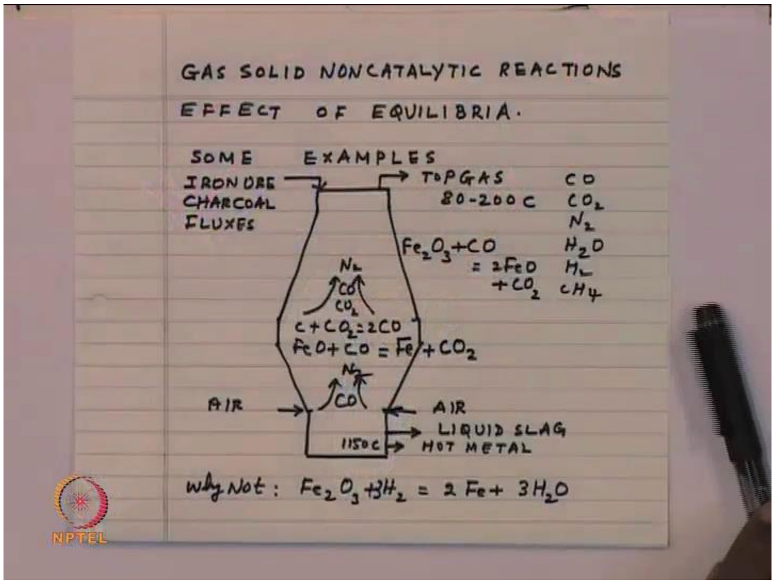

GAS SOLID NONCATALYTIC REACTIONS

EFFECT OF EQUILIBRIA.

SOME EXAMPLES

$Fe_2O_3 + CO = 2FeO + CO_2$

$C + CO_2 = 2CO$

$FeO + CO = Fe + CO_2$

why Not : $Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$

Blast furnace technology is rather new perhaps last fifty sixty years but still making has been known for a very long time. For example, I mean if you look at the history of India for example, there is lot of reports that is available around the world when it says that India was the largest exporter of steel. Now why is it that that you know this people is been able to make so much of steel is because raw materials are available and so on. Now to be able to get good quality steel, we just look at some other reaction that is taking place here. We have iron oxide in the form of iron ore, it is coming in.

You have charcoal is the reducing agent and some flux has to take care of some other reactions and then as this material keeps moving down and more and more reactions take place and then the reaction; for example, iron oxide reacts with carbon monoxide to give you ferric oxide and then carbon dioxide as goes down and found, you find finally this iron oxide reacts with co and finally give you iron and then carbon dioxide, and finally, molten metal's comes out. But the traditional process of steel making in India was very, very different. For example, what is seeing around the world today is that you get a hot metal and because the hot metal, I am just protected by slack certain amount of dissolution of this material also take place in the hot metal and will create certain problems in the point of view using this iron.

But the traditional process that was happening in India was that this ion Fe was actually harvested as a solid and not as a liquid. This is what was unique about the Indian process. I mean in very old perhaps going on for last thousand years and even more interesting perhaps, some of you may not know is that beginning may be fourth or fifth century AD to as late as fifteen hundreds. All the wars particularly in Europe and west Asia were fought with what is called as the Damascus sword and the steel that was used for this Damascus sword world was actually made in some places around Andhra Pradesh and from where it is exported for a very very long time.

On other words, this technology of steel making that is traditional to India is interesting is that they were making solid ion rather than liquid ion. So, on other words, what we are trying to say is that if you know how to handle the equilibria, then we can drive the reaction in the appropriate direction. It is something that we all know and something that our you know people I mean created this process have understood this, and we want to quantitate this by looking at some more example; let me just quickly put down the next example which is also very familiar to you which is calcium carbonate decomposition.

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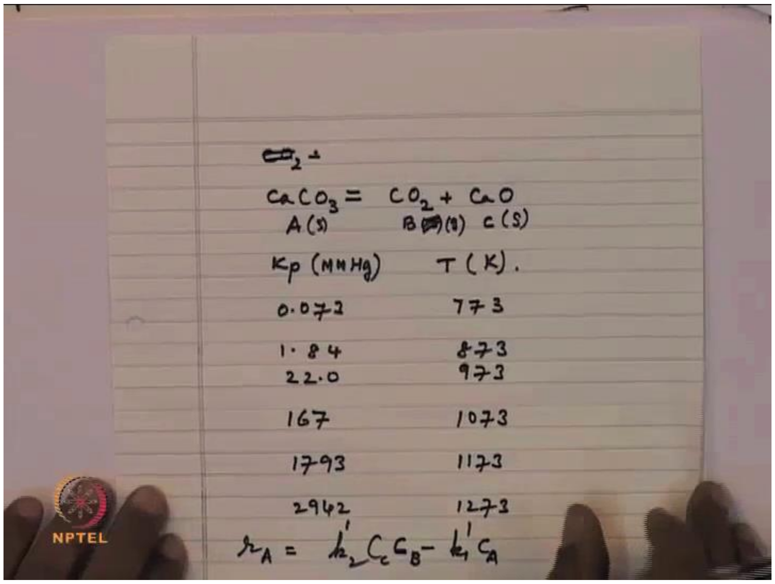

~~CO_2~~ =

$CaCO_3 = CO_2 + CaO$

A(s) B(g) C(s)

Kp (MMHg)	T (K).
0.072	773
1.84	873
22.0	973
167	1073
1793	1173
2942	1273

$r_A = k'_2 C_C C_B - k'_1 C_A$

CaCo3 giving you CO 2 plus Cao; I call this as A; i call this as B; I call this as C, okay. Let me write down the k p for the reaction at different temperatures. Kp is in MMHg, T is in Kelvin 0.073 1.84 22.0 167 1793 2942, 773 873 973 1073 1173 1273, okay. Let me write down the rate of formation as k 2 times cc minus k 2 dash cb times cc minus k 1 dash ca. So, this r a refers to the formation of calcium carbonate, so that k 2 dash cc cb minus of k 1 dash ca, okay. Now since this is a solid, this is a solid and we take solid as a unit activity, of course, in actual practice c is solid and b is gas, sorry okay. Now if you take solid us unit activity we can simplify this.

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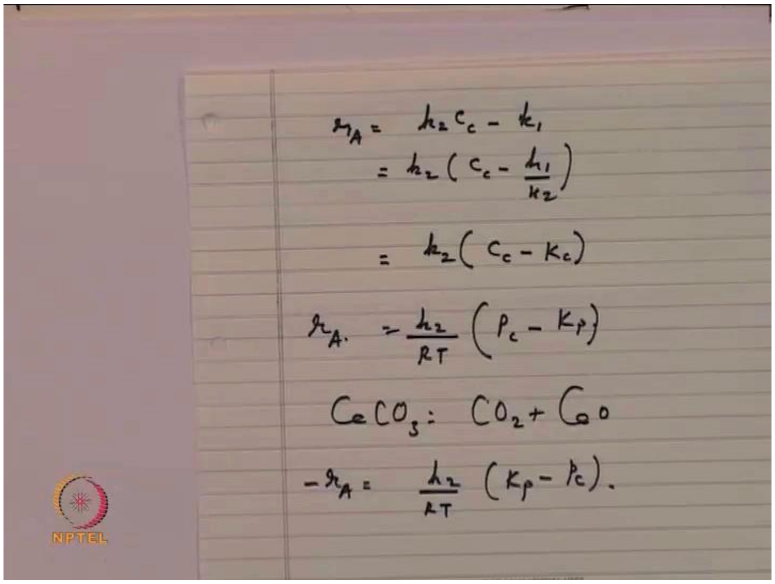

$$r_A = k_2 C_c - k_1$$

$$= k_2 \left(C_c - \frac{k_1}{k_2} \right)$$

$$= k_2 (C_c - K_c)$$

$$r_A. = \frac{k_2}{RT} \left(P_c - K_p \right)$$

$$CaCO_3 : CO_2 + CaO$$

$$-r_A = \frac{k_2}{RT} (K_p - P_c).$$

Let me just quickly write that down. So, with solid as unit activity of r A becomes k 2 cc minus of k 1 or I will put this is as k 2 times cc minus of k 1 divided by k 2, okay. Let me simplify it further which is k 2 times cc minus of k c and I will write it as k 2 by RT pc minus of kp, okay. So, the rate at which the decomposition reaction CaCO3 equal to co2 plus cao takes place really depends; therefore, the decomposition reaction takes place? When the formation takes place when pc is greater than kp; therefore, the decomposition takes place when kp is greater than pc, is it clear. So, the most important thing is that when pc what do we conclude from here? Ra refers to rate of formation of calcium carbonate.

So, when would calcium carbonate formation take place? When pc is greater than kp. When would the reverse reaction takes place? So, we say minus of r a equal to k 2 by r t k p minus of pc, okay, is it all right. So, the decomposition reactions take place when the choice of k p is such that this term is positive, is this point clear to all of you? So let us look at this one again. So, if you look at the k p values for decomposition, we find that around 1073 k, k p value is about 167, correct. Now the partial pressures of carbon dioxide in combustion gas are something like nine percent, ten percent. So, it is about sixty 65 to 70 mm is what we expect in the combustion gases. Therefore, if reaction has to take place at all, then the temperature at which we must perform this must be greater than about 65 mm which means you must choose temperatures around 1073 at least to give us the driving force for the decomposition.

So, this is why you will find in all the lime kills around the world; the temperatures are well about 1073 well above, okay. Now if you look at this planet earth, all of you know that carbon dioxide in this planet is primarily present in rock; that means all the carbon dioxide is present in the form of calcium carbonate rocks. If you go to the martial atmosphere, carbon dioxide is in the atmosphere; that is how its whole thing is organized. That means depending upon this k p values, you will find the carbon dioxide exist in appropriate forms in different planets in the world of the universe.

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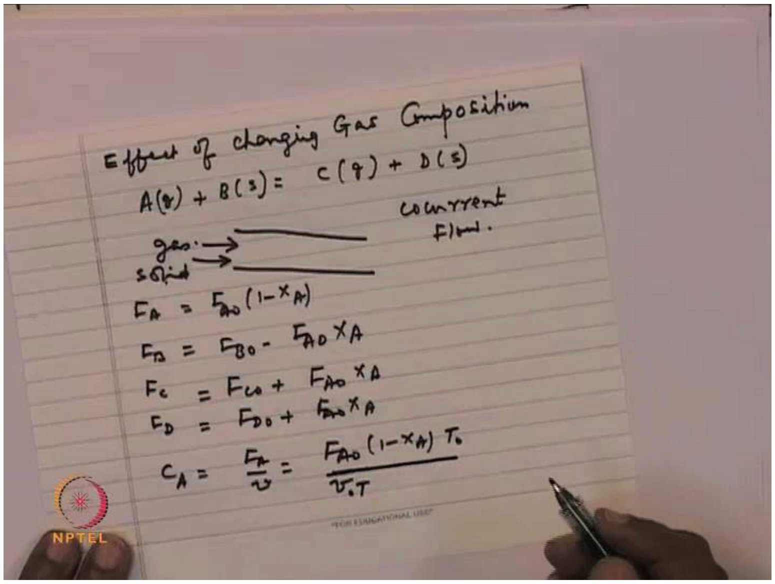

Effect of changing Gas Composition

$A(g) + B(s) = C(g) + D(s)$

cocurrent Flow.

$F_A = F_{A0}(1 - x_A)$

$F_B = F_{B0} - F_{A0} x_A$

$F_C = F_{C0} + F_{A0} x_A$

$F_D = F_{D0} + F_{A0} x_A$

$C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - x_A) T_0}{v_0 T}$

Effect of changing gas composition; now the context to this, let me put it down once again. The context to this is as follows.

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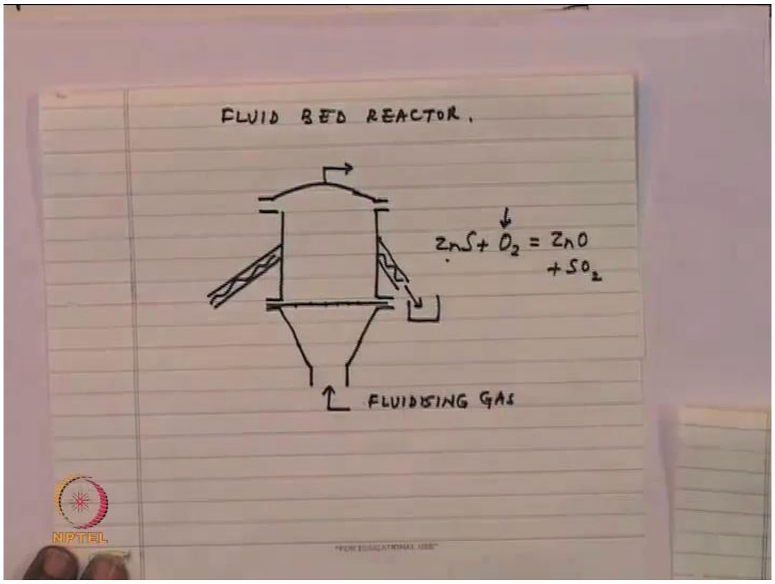

Let us say you are conducting a reaction like a zinc sulfide; zinc blend is the very important ore. In this country, it is available in Udaipur area Hindustan zinc which is used to be now it is owned by Vedanta group. So, they oxidize zinc sulfide with oxygen make zinc oxide. So, you get sulfur dioxide. So, what is it that they do? They have a fluidize bed in which they contact the zinc sulfide is fed like this and here it is coming like this; it gets oxidize and so on. So, what is important here is that the effect of the composition which means effect of what is the oxygen concentration that is in contact with zinc sulfide is important for the rate of chemical reaction.

We must be able to understand this, so that we want to put those numbers in the appropriate perspective. So, let us say the reaction is a gas plus bb solid giving you c gas plus d solid, okay. Let us assume that it is in contact; for the moment we have gas and you have solid. That means gas and solid for the moment, it is in concurrent flow; of course, we can look at where are other features later on concurrent flow, alright. So, our stoichiometry if you put down the stoichiometry f a f b f c and f d are usual nomenclature nothing new here 1 minus of x a f b 0 f a 0 times x a f c 0 plus f a 0 x a f d 0 plus f a 0 x a, okay.

So, this is our stoichiometry and we notice that if you want c a it is simply f a bv v, okay. So, this is f a 0 in our nomenclature divided by v. We take v as v naught taking the Gauss law into account v naught v naught it becomes t by t naught, correct, alright. This is the effect of the temperature on gas flow and so on, okay. Similarly, we can do for others.

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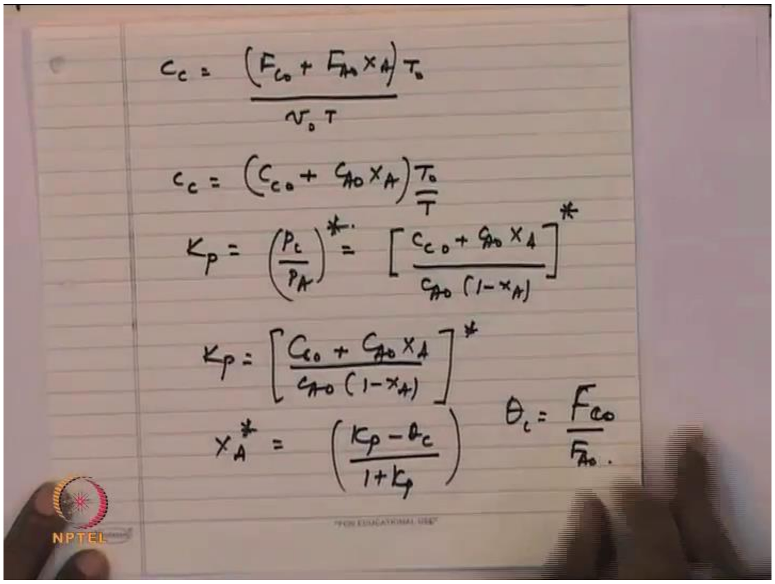

$$c_C = \frac{(F_{C0} + F_{A0} x_A) T_0}{v_0 T}$$

$$c_C = (c_{C0} + c_{A0} x_A) \frac{T_0}{T}$$

$$K_p = \left(\frac{p_C}{p_A}\right)^{*} = \left[\frac{c_{C0} + c_{A0} x_A}{c_{A0}(1 - x_A)}\right]^{*}$$

$$K_p = \left[\frac{c_{C0} + c_{A0} x_A}{c_{A0}(1 - x_A)}\right]^{*}$$

$$x_A^{*} = \left(\frac{K_p - \theta_C}{1 + K_p}\right) \qquad \theta_C = \frac{F_{C0}}{F_{A0}}.$$

Let us do for others c a and c c; c c equal to f c 0 plus f a 0 x a times t naught divided by v naught times t. So, c c becomes c c 0 plus c a 0 x a times t naught by t, okay. Now we just want to see how the equilibria affect the process. So, we recognize that k p for this reaction; for this reaction let us look at it once again. For this reaction, k p is p c by p a; that is what I have written here p c by p a, okay. So, k p is this. Now this is written as this form c c 0 plus c a 0 x a divided by p a which is c a zero times 1 minus of x a. So, at equilibria I am putting a star to denote its equilibria; accordingly, we get k p now depends on c c 0 plus c a zero times x a divided by c a 0 times 1 minus of x a; it is at equilibria.

So, this gives us x a star; this value is simple arithmetic so divided by 1 plus k p, okay, where theta c is simply f c 0 divided by f a 0. Now what we trying to say here is that the value of x a star at the solid surface depends on the choice of theta c. On other words if the product what is our product. Please recognize here our product is c; if product is present in the feat, it has a bad effect on the process because it affects the extent to which we can drive the reaction at equilibria. So, this is one important message that we all know from a basic thermodynamic that is stating the whole thing once again, okay.

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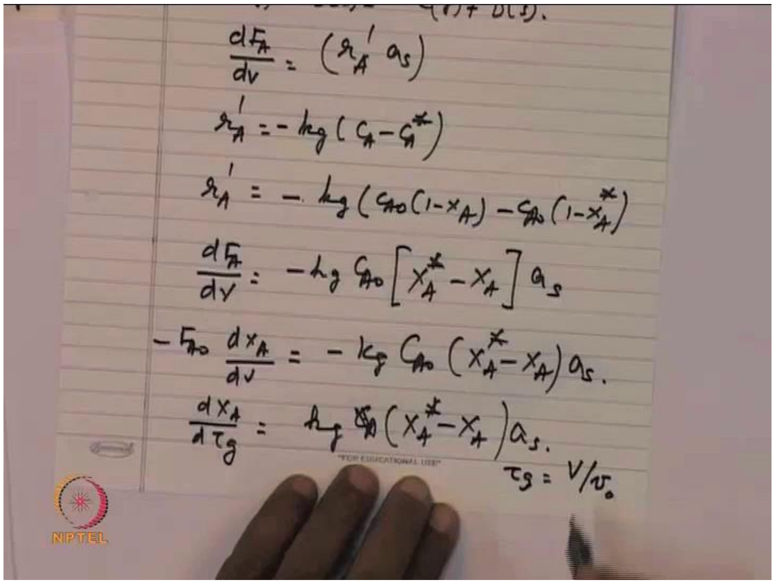

$$\frac{dF_A}{dv} = (r_A' a_s)$$

$$r_A' = -k_g (C_A - C_A^*)$$

$$r_A' = -k_g (C_{A0}(1-x_A) - C_{A0}(1-x_A^*))$$

$$\frac{dF_A}{dv} = -k_g C_{A0} [x_A^* - x_A] a_s$$

$$-F_{A0} \frac{dx_A}{dv} = -k_g C_{A0} (x_A^* - x_A) a_s.$$

$$\frac{dx_A}{d\tau_g} = k_g \cancel{C_{A0}} (x_A^* - x_A) a_s.$$

$$\tau_g = V/v_0$$

Now let us look at the chemical reaction. A gas plus b be solid equal to c gas plus d solid; this is the reaction we are considering. So, the rate at which reaction occurs, we want to do it in this cocurrent flow in a rotary kill; for example, it is r a dash times a s, okay. What is r a dash? R a dash is the rate of chemical reaction per unit surface area and a s is the surface area per unit volume. So, that is how and if r a dash is due to a film diffusion control of which we have talked about earlier. So, it is taking a form of this nature; therefore, you will get r a dash equal to minus of k g; I forgot a minus sign here, yeah, k g times c a 0 times 1 minus of x a minus of c a naught times of 1 minus x a star.

So, this is the rate at which reaction occurs and I have to multiply it by, okay; this is r a, okay. Therefore, d f a which is the rate at which chemical reaction takes please in our equipment is now kg c a naught within brackets of x a star minus of x a multiplied by the surfaces area per unit volume, okay. Now this x a star we have already said let me put this in this form d x a by d v with a minus sign equal to with a minus sign kg c a 0 time x a star minus of x a times a s, okay. Now what do we say is that this x a star, we have already shown little earlier if we recall here; the x a star we have already shown is given by k p minus of theta c by 1 plus k p.

Therefore, we are now in a position to tell what will be the rate at which our chemical reaction with occur in the rotary kill in the concurrent flow of gas and solid, okay. Now also recognize that this x a star depends upon the choice of temperature; it depends on the choice of the conditions under which you will run the process. If there is product in the feet to that extent, you lose reaction rate, okay. So, the context is that combustion gases contain carbon dioxide, and therefore, you have to deal with the fact that carbon dioxide will have a negative influence on the rate of reaction. Therefore, you have to choose the temperature at which you will run the processes having high k p values, so that the driving forces are satisfactory. That is why people run rotary kills at up something like 1100, 1150, 1200, okay. Now let us take this forward a little.

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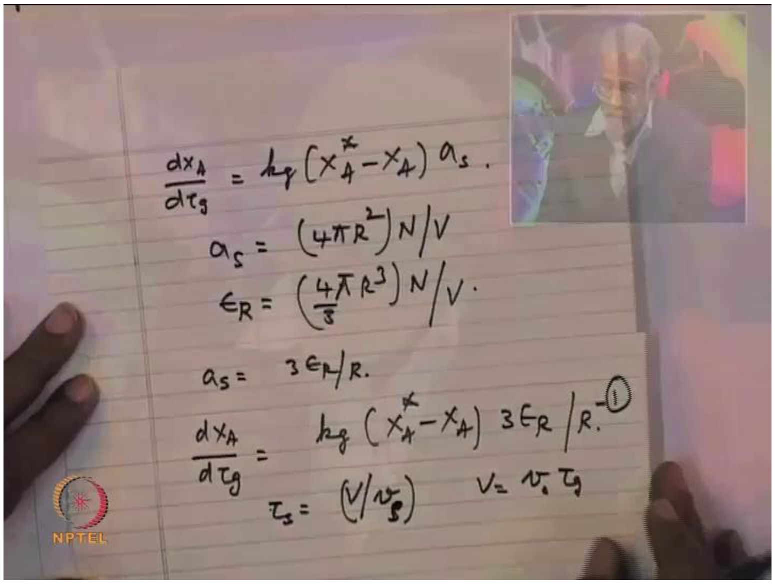

$$\frac{dx_A}{d\tau_g} = k_g (x_A^* - x_A)\, a_s .$$

$$a_s = (4\pi R^2) N/V$$

$$\epsilon_R = \left(\frac{4}{3}\pi R^3\right) N/V .$$

$$a_s = 3\epsilon_R/R.$$

$$\frac{dx_A}{d\tau_g} = k_g (x_A^* - x_A)\, 3\epsilon_R/R. \text{ — ①}$$

$$\tau_g = (V/v_g) \qquad V = v_0 \tau_g$$

We have d x a by please notice that the left hand side can now be written as d x a by d where it is a gas residence time kg c a 0 cancels off. So, you get x a star minus of x a times c a s, okay. So, what is tau g? Tau g is simply gas residence time where tau g is given as sorry tau g is simply v divided by v naught, okay. Now let me restate this equal to k g times x a star minus of x a times a s. What is a s? A s is surfaces area per unit volume; for film diffusion control we are looking at film diffusion control here. Well, the surfaces area which is relevant to the process is the external surface area, okay. So, we said a s is given as 4 pi r square which is the surfaces area of the particle; there are n particles per unit volume of the reaction equipment.

So, this is the surface area of our interest; experimentally we can determine this quantity what is called as 4 by 3 pi r cubed. This is the volume number of particles divided with. Generally for rotary kills in fact for any reacting equipment, this epsilon r is an experimentally determinable number but it means how much solids are held per unit volume of the equipment. Suppose, you stop the rotary kill and then go on and collect all this solids, you will find there are so many you know cubic meters of solid per unit volume you can calculate. Epsilon r is a well-documented number; therefore, depending upon the rotation speed, this number can be obtained.

So, accordingly as can now be written in terms of the epsilon r;, so it comes out to be how much in terms of epsilon r is how much is it? 3 epsilon r by r, okay, is it all right. So, let us substitute for this one here. So, you get k g x a star minus of x a; a s is thrice epsilon r by r, is it okay. If you have a rotary kill in which there is gas and solids are in cocurrent flow it is in a concurrent and flow, then directly this equation will tell us what will be the extent to which we can write the process, okay. So, once you know gas residence time to find out solids residence time, how do you find solids residence time? Solids stress tau s is simply volume of the equipment divided by volume of solids; all the solids you will have to find the volume.

So, this is known. This solid volume is known because you are putting in solids at a certain rate. So, you know the solids volume; you know the reaction volume of the equipment. What is v equal to? V equal to v naught times tau g;, so you can calculate the solids residence times as well, okay. So, given gas residence time data, you can calculate gas solid residence time; therefore, you can specify the whole process on the basis of this equation. Let us say this is equation one, okay.

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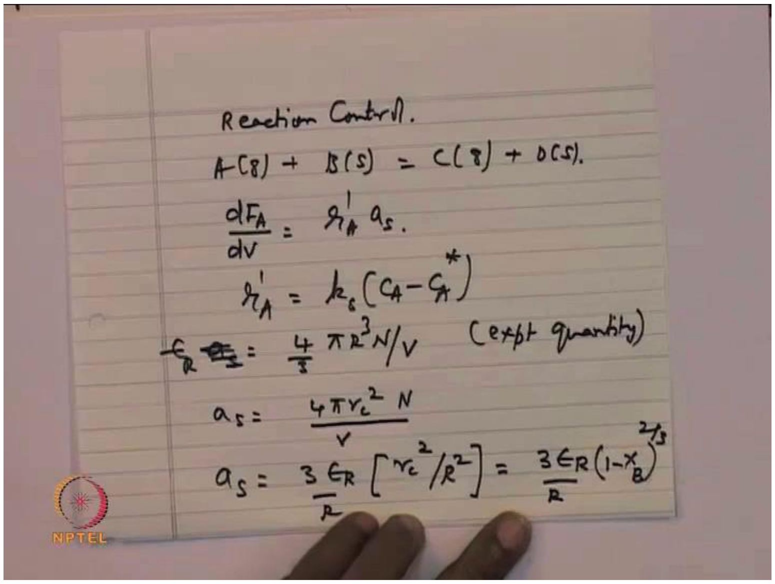

Reaction Control.

$A(g) + B(s) = C(g) + D(s).$

$$\frac{dF_A}{dV} = r_A' \, a_s.$$

$$r_A' = k_s(C_A - C_A^*)$$

$$\epsilon_R \cancel{a_s} = \frac{4}{3}\pi R^3 N/V \quad \text{(expt quantity)}$$

$$a_s = \frac{4\pi r_c^2 N}{V}$$

$$a_s = \frac{3\epsilon_R}{R}\left[r_c^2/R^2\right] = \frac{3\epsilon_R}{R}(1-X_B)^{2/3}$$

If instead of gas film control, suppose let us say you have a reactions control process; what do you have? You have a gas plus b be solid giving you c gas plus d solid, is it alright, d solid, correct. Now if it is under the reaction control, once again our basic equation that describes our process is r a dash times a s, okay. What is r a dash for reaction control? R a dash for reaction control look something like this is k s times c a minus c a star, okay. Once again the form is identical to what we have written for film diffusion control, and what is a s for reaction control? We have said this before; it is 4 by 3 pi r cube n divided by v, is this correct; this is epsilon r.

So, a s is 4 pi r c square n divided by v, okay, is this okay. This is a s, and this is epsilon r. This is an experimentally measured experimental quantity, alright; this is an experimental quantity. So, this comes from experiment a s for reaction control is 4 pi r square n by v, okay. So, we can simplify this and now write a s as thrice epsilon r divided by r within brackets of r c square by r square, is it alright. So, this I will simplify this as thrice epsilon r divided by r 1 minus x b to the power of 2 by 3, is it ok now, alright.

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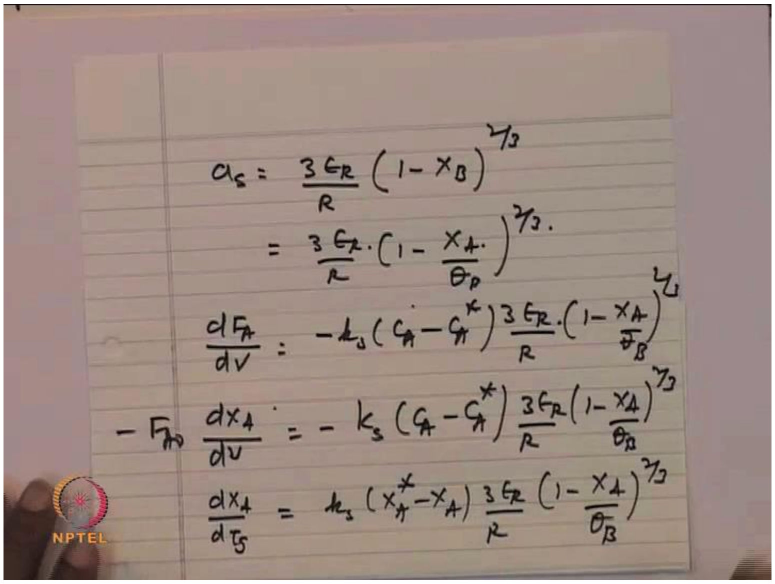

$$a_s = \frac{3\epsilon_R}{R}(1 - x_B)^{2/3}$$

$$= \frac{3\epsilon_R}{R}\cdot\left(1 - \frac{x_A}{\theta_B}\right)^{2/3}.$$

$$\frac{dF_A}{dV} = -k_s(C_A - C_A^*)\frac{3\epsilon_R}{R}\cdot\left(1 - \frac{x_A}{\theta_B}\right)^{2/3}$$

$$-F_{A0}\frac{dx_A}{dV} = -k_s(C_A - C_A^*)\frac{3\epsilon_R}{R}\left(1 - \frac{x_A}{\theta_B}\right)^{2/3}$$

$$\frac{dx_A}{d\tau_g} = k_s(x_A^* - x_A)\frac{3\epsilon_R}{R}\left(1 - \frac{x_A}{\theta_B}\right)^{2/3}$$

So, let me write a s equal to thrice epsilon r divided by r multiplied by 1 minus of x b to the power of 2 by 3. How is x b related to x a? From our stoichiometry, we have already done this. So, it is simply divided by theta b. So, this comes from stoichiometry, so that now our equation now looks like this d f a by d v equal to k s times c a star c a minus of c a star times a s which is thrice epsilon r divided by r 1 minus of x a by theta b to the power of 2 by 3, okay, with a minus sign. So, r it is d x a by d v f a 0 with a minus sign here equal to minus k s c a minus of c a star thrice epsilon r by r 1 minus of x a by theta b into 2 by 3. So, what is it that we have done identical to what we have done for film diffusion control, similar equation is there for reaction control, okay.

Now we can simplify this and write it in this form of d x a by d tau g; please recognize that it is tau g is gas residence time and c a can be written like this k s times x a star minus of x a multiplied by this effect which is by r 1 minus of x a by theta b to the power of 2 by 3, ok; is this alright, is it okay. So, what are we saying now? If we have reaction control instead of film control, the form of the equation that describes your process is given by the right hand side; k s is the reaction velocity, x a star is your equilibria which is already determined and all the other things refers to the process of epsilon r comes from experiments; capital R is the size of the equipment. So, this can be integrated if you know the initial condition; how do you integrate this? X a equal to zero, tau g is equal to zero; therefore, a forward march this can be integrated and we can get how x a changes with tau g.

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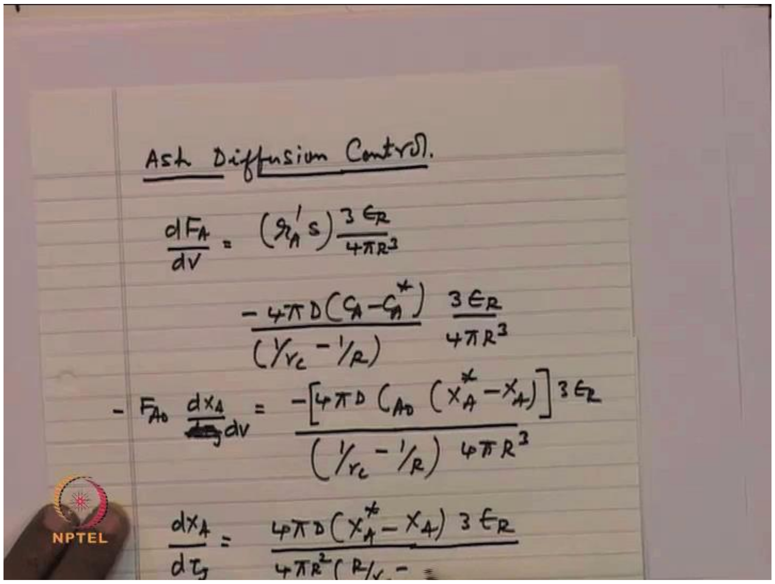

Ash Diffusion Control.

$$\frac{dF_A}{dV} = (r_A' s)\frac{3\epsilon_R}{4\pi R^3}$$

$$\frac{-4\pi D(C_A - C_A^*)}{(1/r_c - 1/R)}\ \frac{3\epsilon_R}{4\pi R^3}$$

$$-F_{A0}\frac{dx_A}{\cancel{d\tau_g}\,dv} = \frac{-[4\pi D\, C_{A0}\,(x_A^* - x_A)]\,3\epsilon_R}{(1/r_c - 1/R)\ 4\pi R^3}$$

$$\frac{dx_A}{d\tau_g} = \frac{4\pi D(x_A^* - x_A)\ 3\epsilon_R}{4\pi R^2 (R/r_c -}$$

Now the third example is the case of what is called as ash diffusion control. What is the ash diffusion control? We talked about it which said that it is the resistance to the supply of gas to the product layer. So, let us write our differential equation once again. We have d f a d v equal to some r a dash times s. What is this r a dash times s? It is the rate per unit per particle. So, I am just multiplying this by thrice epsilon r divided by 4 pi r cubed. Please understand what I am saying. What is epsilon r? Epsilon r is hold up of solids per unit volume, okay. So, that means every unit volumes have epsilon r cubic meters of solids. So, what is the volume of each particle? 4 by 3 pi r cubed; therefore, these 3 epsilon r by 4 pi r cube refers to the number of particles while r a dash s refers to reaction per particle.

So, this is the rate at which reaction occurs per unit volume per unit time, okay. Now what is this r a dash s? We have already done this; we said this is minus of 4 pi d c a minus of c a star. We have done this before, okay, divided by 1 by r c minus 1 by r. We are done this also and then thrice epsilon r divided by 4 pi r cube, okay, is this alright. So, this r a dash s these form we already derived, okay. We have only multiplied by the appropriate number to take care of the number of particles per unit volume, okay. Now we can integrate this; so help me now. So, left hand side becomes f a zero d x a by d tau g with a minus sign equal to right hand side is minus of 4 pi d.

This becomes c a 0 x a star minus of x a divided by 1 by r c minus of 1 by r and put this here thrice epsilon r 4 pi r cube, thank you, okay, is it okay now, is it alright. So, let me write this in this form d x a by d tau g, okay, and the right hand side signs go off, c 0 cancels off. I get 4 pi d x a star minus of x a, okay, thrice epsilon r divided by 4 pi r squared r by r c minus of 1.

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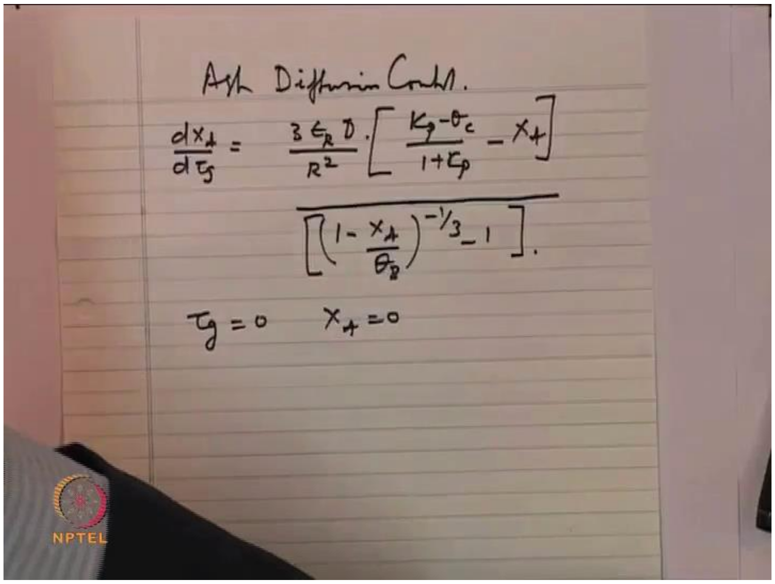

Ash Diffusion Contd.

$$\frac{dx_A}{d\tau_g} = \frac{\frac{3\epsilon_R D}{R^2}\cdot\left[\frac{K_p-\theta_c}{1+K_p} - x_A\right]}{\left[\left(1-\frac{x_A}{\theta_B}\right)^{-1/3} - 1\right]}.$$

$\tau_g = 0 \quad x_A = 0$

So, this d x a by d tau g equal to thrice epsilon r d divided by r squared within bracket. i am just putting this to that x a star in this form minus of x a divided by within brackets 1 minus of x a by theta b, okay, minus 1 by 3 minus of 1, do we all agree with this? From here, r by r c is written in this form, okay, yes or no. This term is r by r c squared is it, r by r c only. R by r c is what; what is r by r c? 1 minus of x b to the power of 1 by 3, okay, and x b is x a divided by theta b comes from stoichiometry, is it alright, yes or n. So, for the case of ash diffusion control, our final form looks like this. This is ash diffusion control, okay.

Now we can integrate this; how do you integrate this? At tau g equal to zero, x a equal to zero, okay. So, therefore, if you have Runge-kutta routine if you want to integrate forward, you only require the right hand side at tau g equal to zero; right hand side is fully known. Therefore, we can forward march and then complete the integration. So, all the three cases case of reaction controls, case of film diffusion control, case of ash diffusion control, we have forms by which we can integrate forward and determine this size of the equipment for a given process that we have chosen, is that clear, okay. Now we can take this a little forward and look at combination of resistances. It is fairly elementary; we have done this earlier but let me run through this once again for the case of ash diffusion control for combination.

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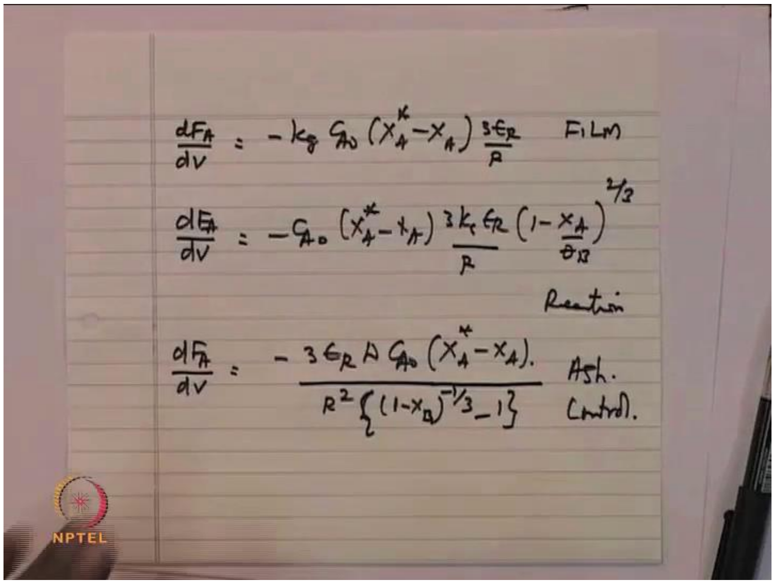

$$\frac{dF_A}{dV} = -k_g C_{A0}(X_A^* - X_A)\frac{3\epsilon_R}{R}$$ FiLM

$$\frac{dF_A}{dV} = -C_{A0}(X_A^* - X_A)\frac{3k_s\epsilon_R}{R}\left(1-\frac{X_A}{\theta_B}\right)^{2/3}$$ Reaction

$$\frac{dF_A}{dV} = -\frac{3\epsilon_R D C_{A0}(X_A^* - X_A).}{R^2\{(1-X_B)^{-1/3}-1\}}$$ Ash. Control.

Let me just put down all the things once again because that makes it little easier equal to minus of kg c a 0 x a star minus of x a; I am just writing it again thrice epsilon r by r. This is for film diffusion, okay; you have done this before. Now I am writing again for the case of reaction control c a 0 x a star minus of x a thrice k s epsilon r by r 1 minus of x a by theta b to the power of 2 by 3; this is reaction control, is it alright, reaction control. Now for the case of what is this? This is ash diffusion control; our numbers looks like this thrice epsilon r d c a 0 x a star minus of x a divided by I am just writing it once again exactly what we have done before 1 minus x b a to the power of minus 1 by 3 minus 1. This is something that we have done just now, okay. So, this is for this is ash control. Therefore, if we have a rotary kill in which all the three are important, how do we combine them? We combine them by recognizing the following.

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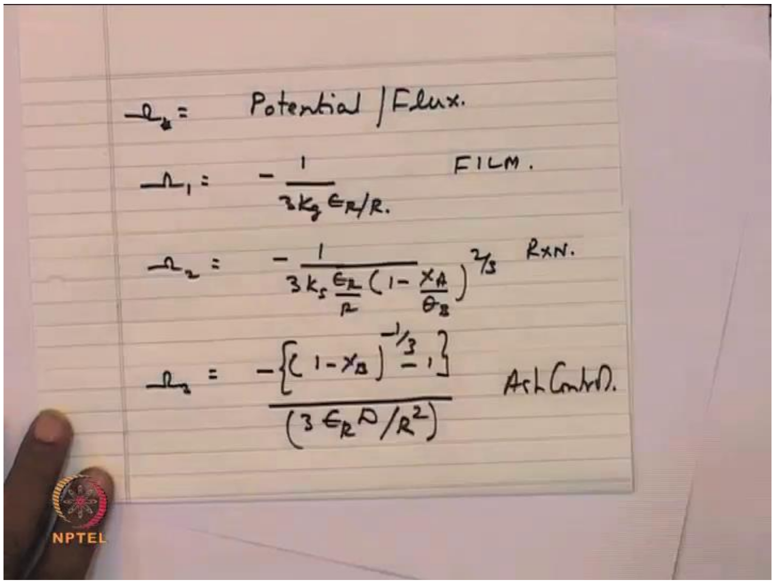

$\Omega_x =$ Potential / Flux.

$\Omega_1 = -\dfrac{1}{3k_g \epsilon_R/R.}$ FILM.

$\Omega_2 = -\dfrac{1}{3k_s \frac{\epsilon_R}{R}\left(1-\frac{X_A}{\theta_B}\right)^{2/3}}$ RxN.

$\Omega_3 = \dfrac{-\left\{(1-X_B)^{-1/3}-1\right\}}{\left(3\epsilon_R D/R^2\right)}$ Ash Contrl.

We write resistance equal to potential by flux. So, for the case of film diffusion, our resistance this becomes 1 by thrice k g epsilon r by r. Please look at the form here; that means thrice kg epsilon r by r, is this clear? I am just writing the resistance by looking at this form itself, okay. The resistant is potential divided by flux; therefore, it becomes 1 by with a minus sign kg thrice epsilon r by r. Similarly, for the next case which is film and reaction, let me write this is for film, okay, and epsilon omega 2 I am writing it as 1 divided by thrice k s epsilon r by r, okay, within brackets 1 minus x a by theta b to the power of 2 by 3. This is reaction. Let us just check this once again c s divided by this; it becomes 1 divided by thrice k s epsilon r by r exactly it is what I have written, okay, is it alright

It comes from the previous form please I cannot show both at the same time, but if you look at this here, c a 0 x a star divided by this becomes just inverse of this, okay, and for the third case which is epsilon third that becomes minus 1 minus of x b to the power of minus 1 by 3 minus 1 divided by thrice epsilon r divided by r square. So, this is the form in which the resistance for ash control, okay. So, if you want to combine all the three, our procedure is what is our procedure that flux equal to total potential divided by the total resistance.

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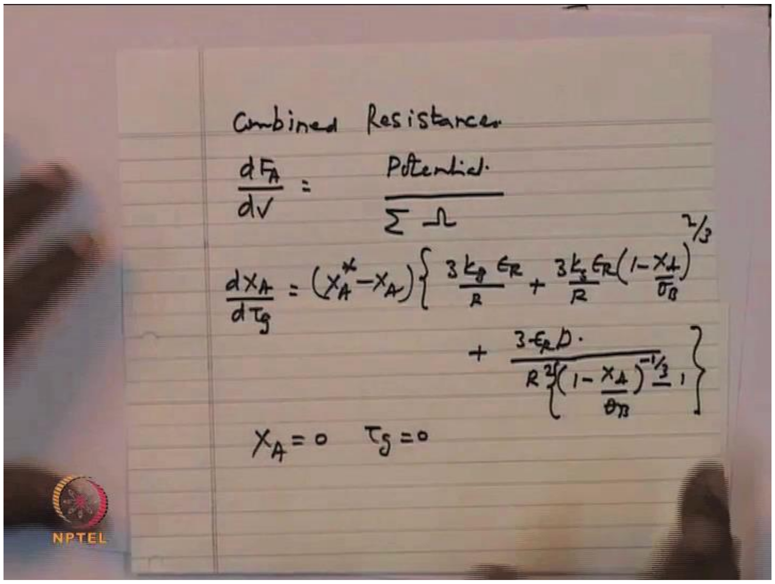

Combined Resistance

$$\frac{dF_A}{dV} = \frac{\text{Potential}}{\Sigma \Omega}$$

$$\frac{dX_A}{d\tau_g} = (X_A^* - X_A)\left\{\frac{3k_g\epsilon_R}{R} + \frac{3k_s\epsilon_R}{R}\left(1-\frac{X_A}{\theta_B}\right)^{2/3} + \frac{3\epsilon_R D}{R^2\left\{\left(1-\frac{X_A}{\theta_B}\right)^{-1/3} - 1\right\}}\right\}$$

$X_A = 0 \quad \tau_g = 0$

So, let me write it in that form which means for the case of combined resistances flux which is d f a by d v should be equal to potential divided by summation of sigma, yes or no? So, once we put all the resistances together, our number looks something like this; I will not write this. In fact, I will write the final form because it is fairly elementary. So, the final result looks like this. It is not necessary to do the whole thing again and again because you have already done that becomes x a star minus of x a within brackets of thrice kg epsilon r by r the first one. Then you have thrice k s epsilon r by r within brackets of 1 minus of x a by theta b to the power of 2 by 3. So, this is reaction.

Third one is ash diffusion which is epsilon r and diffusion coefficient divided by r squared 1 minus x a by theta b. It is a little messy but you know it is something that we have to get used to minus 1 by 3 minus 1, okay, is it alright. So, it is exactly similar to what we have done for single particle. So, if you have rotary kill gas cocurrent flow of gas in solids, the gas conversion with respect to gas residence time is this is the potential divided by resistance, okay. The right hand side once again x a equals to 0 at tau g equal to 0 which means for a forward mass Runge-kutta routine, the right hand side is fully specified; therefore, we can integrate forward and complete the process by whatever is specified the rest of it can be done through the appropriate integration.

Notice here that kg is an experimentally known quantity; k s is a known quantity; diffusion coefficient is a known quantity; epsilon r the holdup is a known quantity, so right hand side everything is known. And therefore, you will be able to determine the extent of reaction for a given residence time, okay. Once gas residence time is known, you know the volume of the equipment and if you know the volume of the equipment, you know the solid's residence time. So, yours process is fully specified, okay. So, far the case of gas solid reaction taking place in a rotary kill under cocurrent flow, we have the process design completely specified, okay.

Now if I ask you what is the way by which we can tell what resistance is controlling out of the three; whether it is film diffusion is controlling, whether it is reaction is controlling, whether it is ash diffusion is controlling, we said one way of knowing this is to try and do an experiment where we change velocities. When you change velocities mass transfer coefficient changes generally to the power of point eight of Reynolds number. So, you will find velocity effects generally affecting the mass transfer coefficient; therefore, if you do three experiments in three different velocities, we will able to tell whether mass transfer is an important resistance or not.

Similarly, if you have control due to chemical reaction, chemical reactions are very strong functions of temperature; you do experiment the different temperatures. You will find that if it is important, then temperature effects will show up because reaction rates will change rapidly because of the choice of temperatures. If it is ash diffusion control, we know that it depends on square of particle size. Therefore, if we choose different particle sizes immediately that effect will come out. Therefore, to discern the importance of controlling regime, we essentially do some experiments to find at what is important, okay. Now having said this, let us look at an example from see we did at.

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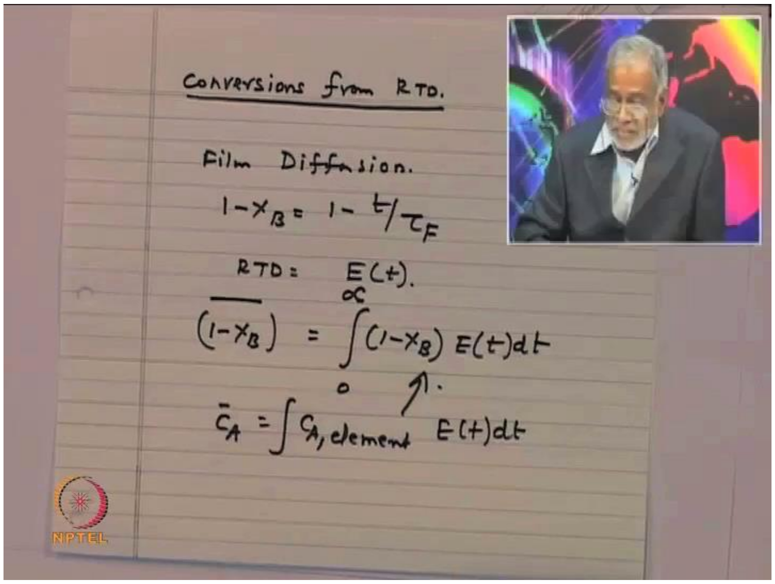

Conversions from RTD.

Film Diffusion.

$1 - X_B = 1 - t/\tau_F$

RTD = $E(t)$.

$$\overline{(1-X_B)} = \int_0^\infty (1-X_B)\, E(t)\, dt$$

↑.

$$\bar{C}_A = \int C_{A,\text{element}}\, E(t)\, dt$$

So, this is conversations from RTD. See what we have done so far if we look here, what is it that we have done so far? Here we said gas and solids are in cocurrent flow and the implicit assumption here is that both are in plug flow. Therefore, the residence times are the same for every particle. This is implicit in this formulation, but this may not be the case. Therefore, we will have to see what can we do in case there is an RTD. The RTD can be for gas, it can be for solids, okay. So, we have done this I just set it down for the case of film diffusion. Let us say there is a single particle and we have said this that if there is a single particle that particle behaves like this; we have derived this, okay.

If there is a single particle and if it reacts and it will react in this form; if you now put this inside reaction equipment, this is reaction equipment where you know that it has RTDs that RTD of the reacting equipment is some e function. Let us say this is known to you; how does it come? It comes from an experiment; we have done these experiments. So, whatever be the equipment, we can determine what is the residence time distribution for that particular. If it is for solids, we do an experiment by putting a tracer on the solid state. If it is for gas, we put a gas tracer; both types of experiments we may have done in our undergraduate course or it can be done. It is not a very difficult experiment to do.

On other words, we know what is the residence time distribution. Now what is that we want? We want so we have 1 minus of x b equal to 1 minus of x b 0 to infinity, can we say this? We said this is the context of what we have said so far is just recall what we have said? We said c a average equal to c a element multiplied by e t d t, okay exactly what I have written, okay; same thing is being written. So, the average you will see is each particle multiplied by the e t d t of that particle, okay. Now what happens in a gas solid reaction is that let us recognize that once again.

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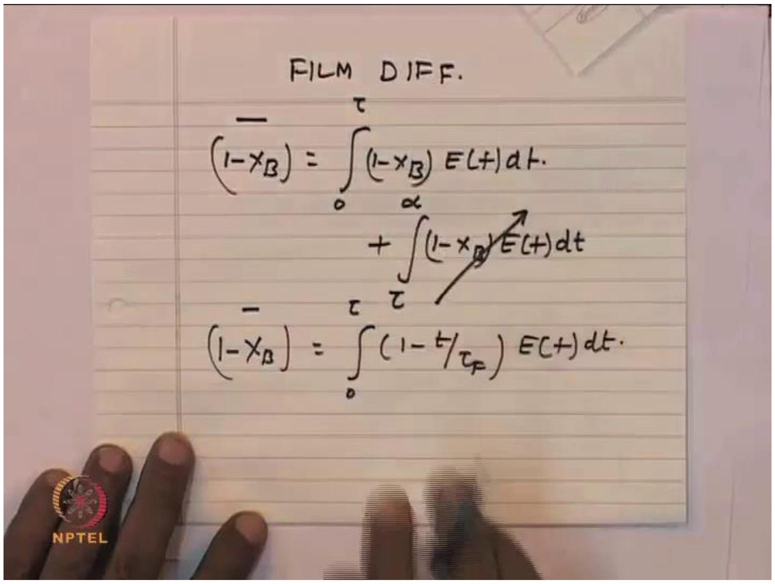

FILM DIFF.

$$\overline{(1-X_B)} = \int_0^{\tau} (1-X_B)\, E(t)\, dt.$$

$$+ \cancel{\int_{\tau}^{\infty} (1-X_B)\, E(t)\, dt}$$

$$\overline{(1-X_B)} = \int_0^{\tau} \left(1 - t/\tau_F\right) E(t)\, dt.$$

In a gas solid reaction we have 1 minus of x b equal to 0 to tau 1 minus of x b e t d t plus tau to infinity 1 minus of x b e t d t; can I write this? Now what happens to this integral tau to infinity 1 minus of x b e t d t; what happens to this integral? We know that at tau x b is 1; therefore, 1 minus of x b is 0 for all particles with time of residence greater than tau. Therefore, the second integral goes to zero; therefore, in gas solid reactions where the time for complete consumption is finite, the integral has to go from 0 to tau and not 0 to infinity, is this clear, okay. So, recognize that the integral goes from 0 to tau and not 0 to infinity. What we have said is that this integral 0 to infinity have broken up and 0 to tau and tau to infinity, okay.

Now 1 minus of x b, what is the value of 1 minus of x b for time of residence greater than tau; every particle is fully converted for the time of residence greater than tau. Therefore, 1 minus of x b for that particle is zero; therefore, the second integral is identically zero. Therefore, the second integral disappears, is that clear, yes or no 1 minus of x b is 0 because the time of residence is greater that tau. When time of residence is greater than tau, the particle is fully consumed fully reacted; x b is 1. Therefore, 1 minus of x b is 0; therefore, 1 minus of x b e t d t is 0. Therefore, we delete that term, okay.

Therefore, 1 minus of x bar b which is the average extent of reaction you will find on the particle is 0 to tau of 1 minus of x b e t d t. What is 1 minus of x b for the case of film diffusion control? We have already written 1 minus of x b, we have said it is 1 minus t by tau f; it has come from our single particle analysis. Therefore, 1 minus of x bar b equal to integral 0 to tau 1 minus of t by tau f e t d t, is this alright. What is the first term? First term is how the particle behaves, okay; what is the second term? Second term talks about how much time this particle is spending in the equipment, and it is this product which gives you the average, is this clear.

First gives you the behavior of that particle; second term gives you how much time the particle is pending in the equipment. Therefore, that product gives you the average integrated over 0 to tau, is this clear. So, that is what is this whole thing about, okay. Now you have done for the case of film; this is for film diffusion control, okay, and similarly, you can do for reaction control and so on.

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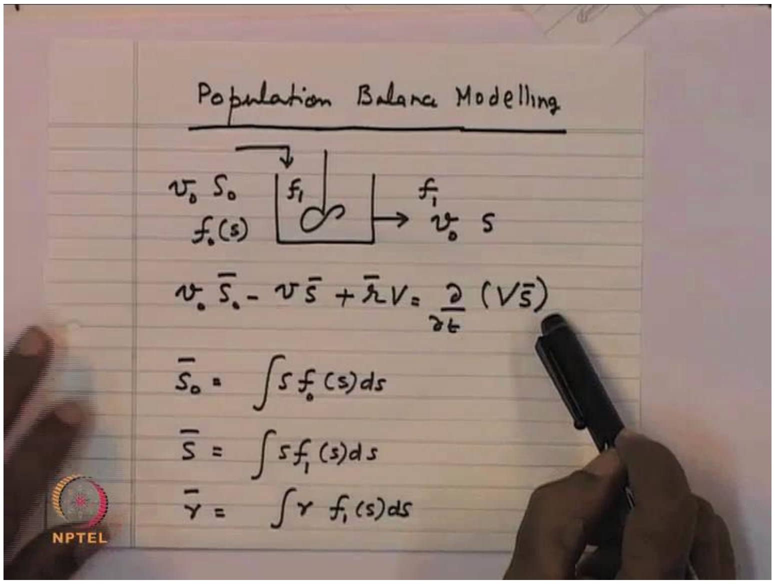
Population Balance Modelling

$$v_0 \bar{S}_0 - v\bar{S} + \bar{r}V = \frac{\partial}{\partial t}(V\bar{S})$$

$$\bar{S}_0 = \int s f_0(s)\,ds$$

$$\bar{S} = \int s f_1(s)\,ds$$

$$\bar{r} = \int r\, f_1(s)\,ds$$

See I just want to begin what is called as population balance modeling. See if you look at a chemical reaction particularly with respect to particulates like gas solid reactions; while solids are moving, gas is moving and we want to understand how this solids how much time it is spending in the equipment; how much time gas is spending in the equipment. So, basically we want to get more clarity on what happens to each element that is going into the equipment. So, this is very nice technique and I want to present this in the simplest form; there are lot of material in the literature in this simplest form. I have taken an example a simple example to illustrate what we want to do, okay.

Now we have been talking about stir tanks for a long time, correct. So, what do we have in stirred tank? We have a fluid entering the equipment at some flow and there is some concentration whatever that may be and comes out at some other concentration because of the reaction, correct. Now if I ask you, what is this s naught; what will you tell me? We will say it is concentration of material that is entering the equipment. Suppose, I ask you how do you know what that number is; you will answer saying that it is I have measured this. This is the measurement that I have done by taking samples, okay. Now we write our material balance, we write like this. This is how we generally write our material balance.

So, this is a material coming in; this is material going out. This is the material that is generated, and this is what is the accumulated, okay. Now what I want to say now, you do not have to agree with me, but the argument is like this. What we are measuring is not s naught, we are measuring some average; what we are measuring is some average, would you agree with me? Any measurement we are doing is an average of the samples we have taken. What I now want to say is that this number that we are measuring is actually this. What is f naught? The f naught is the distribution of that property s of which we have taken samples. There are many fluid elements in our sample and what we have measured is some average, and that average is defined as the first moment of the distribution, is this clear to what we are saying.

Every measurement we do is an average, and that average is obtained by integrating the distribution property first moment of the distribution property. Therefore, if f naught is the distribution of this property s at the feet; therefore, the average we measure is actually integral s f naught of s d s. Similarly, what we measure on the other side is I will call this as f s. I will put this as f 1; our nomenclature is f 1, is it okay, yes or no, is it okay, alright. How do we understand this r bar? We understand r bar equal to integral r f 1 s d s, is it okay. The meaning of r bar what is f 1 at the exit is also the f 1 in the equipment; that is the meaning of a stirred tank. We are looking at a stirred tank; we will relax all this as we go along, we will look at other situations where you can take care of all this.

For the moment, f 1 at the exit is same as f 1 in the equipment; that means the distribution of the property that we are trying to understand, it is the same inside the equipment as it is at the exit, because that is the property of stirred tanks, is it ok, alright. So, what I want to do now is put this definitions. What I want to do now is that now that we know what is s naught what is s bar and what is r bar, we can substitute in this equation, yes or no.

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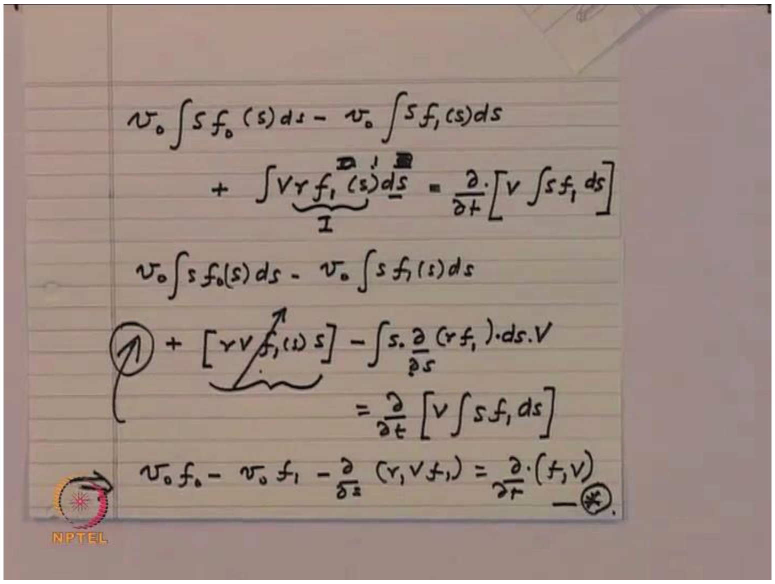

$$v_0 \int s f_0(s)\,ds - v_0 \int s f_1(s)\,ds$$

$$+ \int V \underbrace{r f_1(s)}_{I} \, ds = \frac{\partial}{\partial t}\left[V \int s f_1 \, ds\right]$$

$$v_0 \int s f_0(s)\,ds - v_0 \int s f_1(s)\,ds$$

$$① + \left[r V f_1(s)\, s\right] - \int s \cdot \frac{\partial}{\partial s}(r f_1) \cdot ds \cdot V$$

$$= \frac{\partial}{\partial t}\left[V \int s f_1 \, ds\right]$$

$$v_0 f_0 - v_0 f_1 - \frac{\partial}{\partial s}(r_1 V f_1) = \frac{\partial}{\partial t}(f_1 V) \quad - (*)$$

So, let us substitute and see how it looks like. So, let me replace v naught integral s f naught s d s minus v naught integral s f 1 s d s, okay, plus integral v r f 1 s d s equal to del by del t of v s f 1 d s. I will put there is no space here. So, I will write like this, is it alright what I have written; have you written it correctly? Please tell me. Now what I am saying is that I will call this I want to integrate by parts. I want to integrate see this integral I want to integrate by parts. So, this is d s is our second function and this is the first function. So, integrating by parts please help me; let me just write down and you tell me whether what I have done is right. I am integrating by parts; I am writing the first two terms as such no change.

Now I am integrating by parts. So, first function is the integral of the second. So, I write this as first function into integral of the second; I have written it like this r v f 1 s times s, okay, minus integral of differential of the first. Differential of the first is s del by del s r f 1, is it alright what I have written? Yes, please tell me, is it okay. Is this integration correct and then equal to right hand side del by del t because all the rest is very straightforward once we are clear about this, then all the rest is very straightforward, clear, ok fine, alright; that is the mistake I made. So, first function into integral of the second, correct, okay.

Now what I have done is the following. What I am saying now is that let us look at carefully what is this term. First term is s f naught s d s; second term is s f 1 s d s; third term this term minus of s naught del by del s of this whole term, correct. Now what I am saying is please tell me whether I will do it correctly; I will just write this. Please observe what I am writing f naught minus of v naught f 1 minus of del by del s of r 1 v f 1 equal to del by del t of 1 v. What I am saying is this equation this equation here is first moment of this equation, do we agree? Suppose you take first moment of this equation, do you get this? What is first moment? You multiply by s and integrate over the interval.

First moment of this equation is what we have got about, is it alright; we all agree with this. First movement of this equation I call this equation as star, then I say that first moment of star is what I have written above; do we all agree with this, yes or no, okay. You see carefully first moment of this is this excepting that this term is extra from this first moment of this; this term is coming out as extra, is this clear. I am going to delete that term for the moment; we will talk about it later. For the moment I am going to delete this term; I will give reasons for it a little later. So, what I am saying is that equation star represents a more fundamental statement of conservation. So far, we have always talked about conservation by talking about averages.

Now we have an equation which talks about the distribution of the property which means now if you have a population if you know the distribution of the property of interest in that population, then we can now understand how the distribution changes because of whatever happens inside the population, okay. It can be birth; it can be death; it can be grow whatever various kinds of things at happen in a population we can understand. So, this is the fundamental statement of what we call as population balance modeling. You will find in population balance literature, people will starts with this equation, okay.

They will give you no proof; this is this equation is assumed. What I have tried to do is that how this comes from our basic understanding of material balance in a stirred tank, okay, and what I have tried to tell you is that there is one term that we have deleted, okay that people delete. They delete this one term and then they write this star as the statement of conservation when we talk about populations, okay. So, hence forth we will write our material balance for population distributions in this form where f will refer to it can be activity of a catalyst, okay, or it can be size of a particle in a process where it is undergoing combustion or it could be you know how if f refers to a share in a market, how this share gets distributed among various people.

So, we can talk about dynamics in an economic systems, various things we can talk about. Really once you understand what is this f, then we can do lot of these things, okay. Now I will prove this term why I have deleted I will prove that shortly as we go long and look at some examples. For the moment, let us assume that this is okay. Now having said this, what people do in the literature I will tell you. So, people do not derive it in this form; this form is it is not derived. Instead they do it in slightly different way; what they do is the following.

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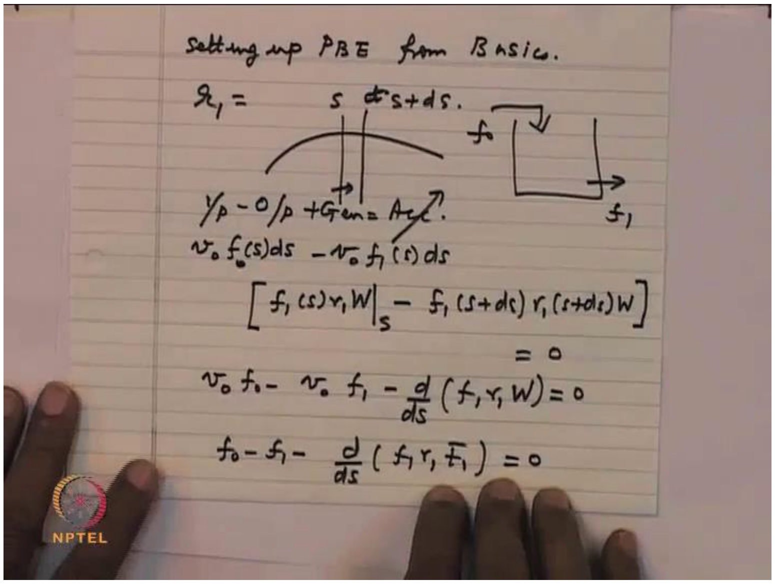

Setting up PBE from Basics.

$r_1 =$ s ~~ds~~ s+ds.

$I/p - O/p + Gen = \cancel{Acc}.$

$v_0 f_0(s)ds - v_0 f_1(s)ds$

$$\left[f_1(s) r_1 W \Big|_s - f_1(s+ds)\, r_1(s+ds) W \right] = 0$$

$$v_0 f_0 - v_0 f_1 - \frac{d}{ds}(f_1 r_1 W) = 0$$

$$f_0 - f_1 - \frac{d}{ds}(f_1 r_1 \bar{t}_1) = 0$$

So, I will this as setting up population balance from basics. So, what they will do is like this. I will call this s; I will call this s plus d s, okay. So, what are we doing? We are trying to look at an interval between s and s plus d s and trying to find out what happens to this interval due to flow and due to reaction, okay. Now what happens to this? So, I am writing the convective flow; convective flow is so much material enters this interval due to convective flow, do we agree, yes or no; do we agree or not what I have written. See we have a stirred tank into which material is entering; this is our stirred tank, this is our stirred tank.

Material is entering, material is leaving; this we say as f naught, this we say as f 1, correct. So, if we take an interval between s and s plus d s, we want to know what happens to this interval because of flow and reaction, okay, because of flow material so much material is entered and once again it is input minus of output plus generation equal to accumulation, okay. For the moment we can write for steady state may be. So, how much material is entering interval between s and s plus d s I say it is v naught f naught s d s, is this clear to all of you? So much material is entering; how much is leaving? V naught f 1 s d s, okay; now what happens to this interval because of reaction, okay.

Let us see our reaction is r 1, okay. So, material the reaction is written like this. So, so much of material at s is entering, so much of material is leaving, can we say that? In the interval between s and s plus d s, so much is whatever reacting at s will contribute s plus d s, correct, r 1; this is that means whatever material is happening at s, it will contribute s plus d s. Therefore, whatever is accumulating between here is this difference is what will accumulate. So, that is equal to this is how our friends will write the population balance in the literature; basically understand this. This is how they will write; that means what is this reaction rate function? It increases the property; the property increases, okay.

Therefore, s contributes s plus d s. It is this difference which will contribute to the interval between s and s plus d s. So, this is how in population balance modeling, they will write the effect of chemical reaction. Now if you take the limits as s tends to 0, our equation will look like this. So, this is how they would write, is this clear. How do we derive the population balance equation for a stirred tank, okay. So, the interesting thing is only this to understand how do we represent the reaction term contributing to the internal between s and s plus d s; this is how it is represented. Whatever reacts at s contributes to s plus d s; whatever reacts and s plus d s goes out. It is this difference which will accumulate in the interval. So, this it is how it is represented, okay.

We have derived the same thing from fundamentals already, okay; previously we derived the same thing from fundamentals, is that clear, but we said we will knock out one term. I have not given you reasons for that; we will come to that shortly. But in the literature they will do it like this and not recognize that there is one term which we have knocked out, is that clear what we are saying. So, basically I mean what they have left out we will prove; that is not wrong, it is okay. But what you will see in the literature is this, okay. Therefore, if you have a stirred tank where the distribution of property at entrance is f naught, the distribution of property at the exit is f 1 and the rate at which the property changes because of this reaction is represented by r 1.

And t 1 bar represents the residence time of that property in the equipment. Now this is what describes how the distribution changes because of chemical reaction, is that clear; we have ran out of time. So, what we will do when we meet tomorrow is that we will go through this once again and then try and apply this one or two situations of practical interest in our process industry, try and understand how we can actually determine the distribution functions, and how those distribution functions are affected by the process parameters, and how they are useful in designing equipment and understanding how the equipment will perform and so on; I will stop there.