Rate Processes

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Module No. # 01

Lecture No. # 01

Rate Processes

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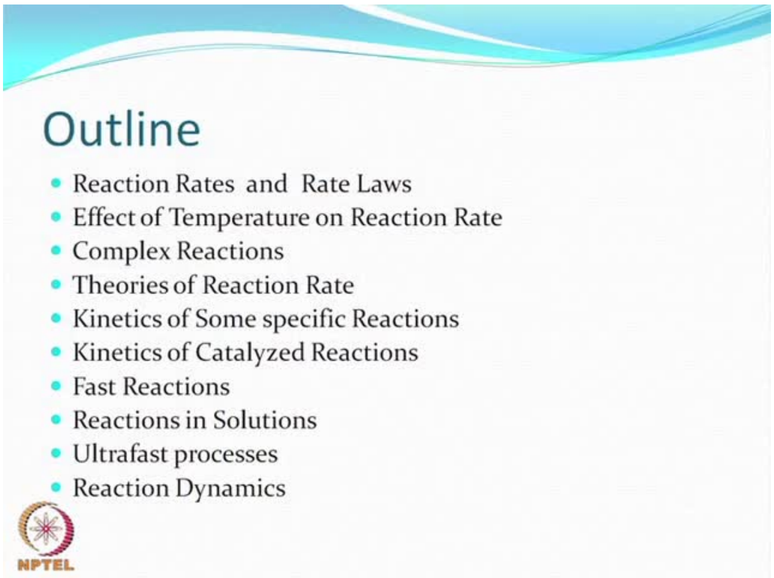

Rate processes, so the topics of this talk, I mean, the whole course is divided into many parts. So, one is the reaction rates and rate laws, next we will talk about effect of temperature on reaction rate, then we will go on to complex reactions; after that, we will move on to theories of reaction rate, kinetics of some specific reactions, kinetics of catalyzed reactions; then we will move on to fast reactions; after fast reactions, we will move on to reactions in solutions, then some modern topics like ultrafast processes and last reaction dynamics.

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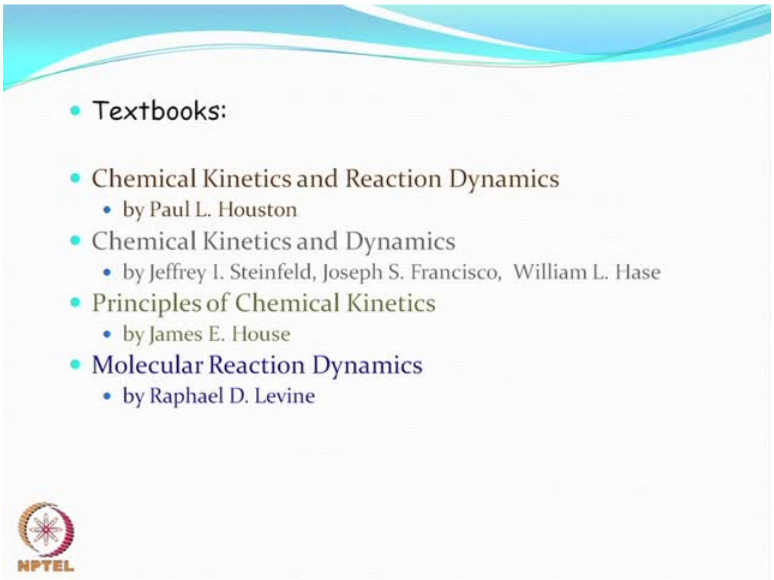

So, I am recommending these text books - one is Chemical Kinetics and Reaction Dynamics by Houston, then another book is by Chemical Kinetics and Dynamics by Steinfeld, Francisco and Hase; third one is Principles of Chemical Kinetics by House and the other book is Molecular Reaction Dynamics by Levine.

Now, apart from these books, any standard physical chemistry text will also help, maybe many other books are available in market, so one can have that also.

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So, chemical kinetics how is that important? Now, chemical kinetics affects everyday life. So, because it determines how fast insects walk, how quickly plants and animals grow and even how fast hair grows on your head and it is also very important in chemical processes. Now, selectivity and activity of chemical reactions determines how well chemical processes work.

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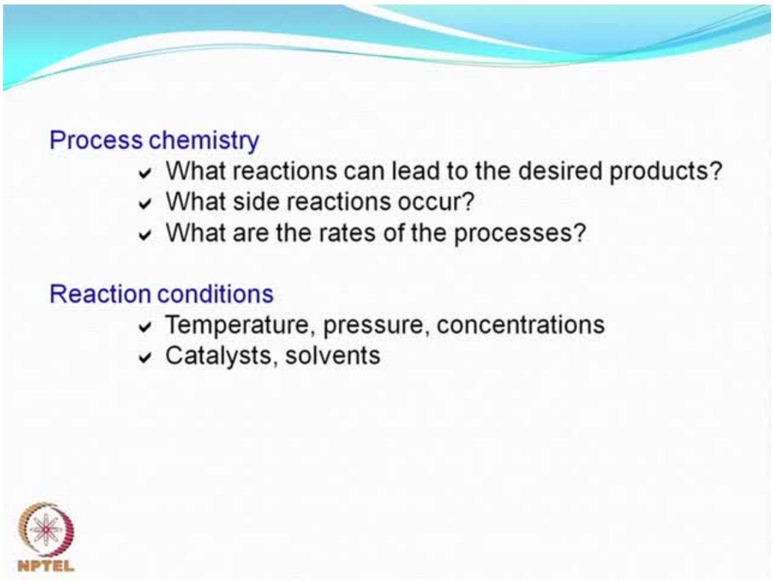

Now, in process chemistry the important parts are like what reactions can lead to the desired products, next is what side reactions can occur and the third one is what are the rates of such processes that are occurring?

Another important thing is reaction conditions; so conditions like temperature, pressure, concentration and catalysts are also important and of course, solvents in which the chemical reactions are carried out; so these are very important. Especially temperature and pressure, these are external factors; so these are very important in chemical kinetics or may be in chemical processes.

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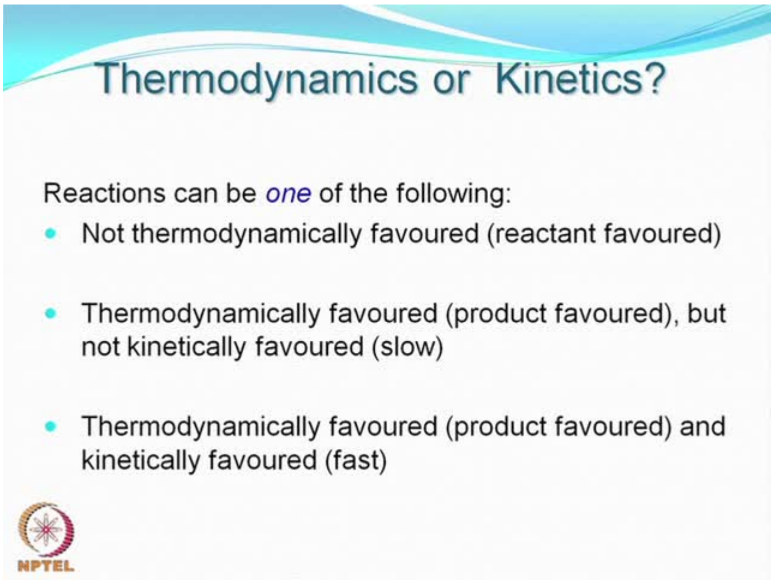

Now, if we think of thermodynamics versus chemical kinetics, now in chemical reactions in case of chemical reactions, these reactions can be one of the following: first one is not thermodynamically favored, maybe it is called as reactant favored; next one is thermodynamically favored, which is also called product favored, but not kinetically favored that is a slow reaction. That is, the kinetics of the process is slow that is why it is called kinetically disfavored, that is, slow kinetics, that is, with time, it is happening slowly; and the third kind is thermodynamically favored, that is, product favored and also kinetically favored, which is fast, that means, it is thermodynamically favorable as also kinetically favored or kinetically loud or kinetically very fast.

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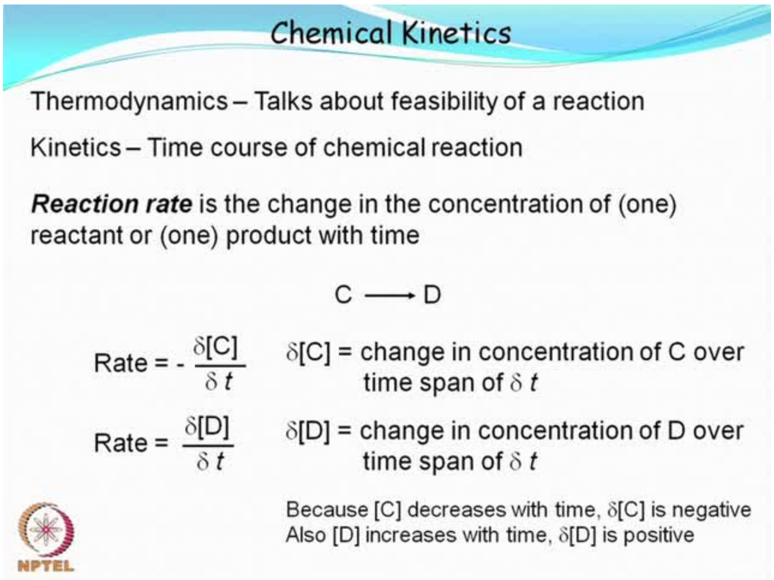

Now, thermodynamics talks about feasibility of a reaction, that is, whether the process that is the chemical process is energetically feasible or not and kinetics talks about time course of chemical reaction. That is with time, how is the process occurring, that is, whether it is occurring fast or it is occurring slowly. Now, reaction rate is the change in concentration of one reactant or one product with time; it is in generally defined in this way.

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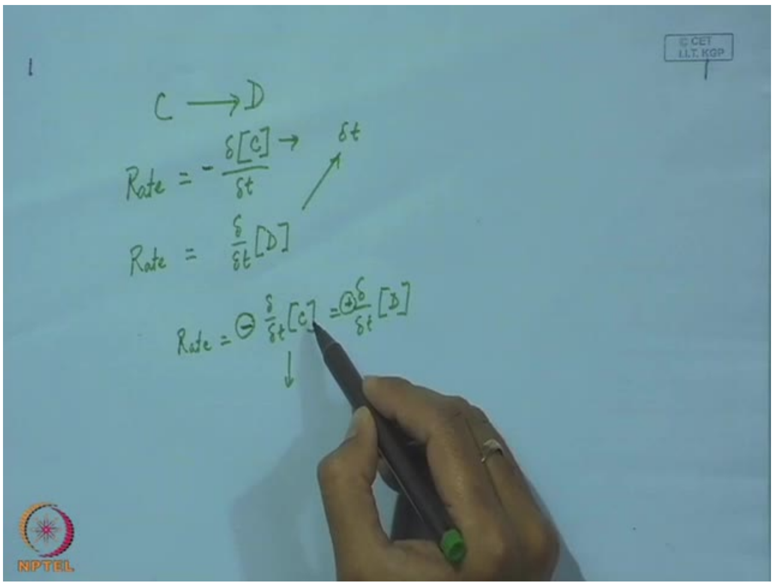

Now, suppose we have got a chemical reaction like C is being converted to D, so that is C to D transformation. So, if we look into time rate of change of concentration of C, then we will write rate is equal to delta, that is, differential quantity delta C or D C dt with a negative sign why it is with a negative sign? Because C is reducing in amount and in the same way if we think of the time rate of formation of D, then rate will also be written as del del t of D.

So, this is also rate; this also rate. So, this is time rate of depletion of C and it is the time rate of formation of D; so where delta C is the change in concentration of C over a time span of delta t.

In the same way, it is the time rate of change of concentration of D although it started from 0, because at 0 time, there was no 0, I mean, there was no D and with time D is increasing in amount. So, we can call that, this delta D is the time rate of, I mean, delta D delta t is the time rate of change of concentration of D, that is, delta D is your change in concentration of D over time spent of delta t.

Therefore, since C is decreasing in concentration therefore, it is a negative sign. So, we can write rate is equal to minus of del del t of C which is equal to del del t of D; remember this negative sign, it is a plus, this is a negative sign; here this is a plus sign, there is no change in sign, but here is a negative sign, because it is decreasing in amount. Therefore, we can express the rate in both ways, in terms of one of the reactants or may be in terms of one of the products.

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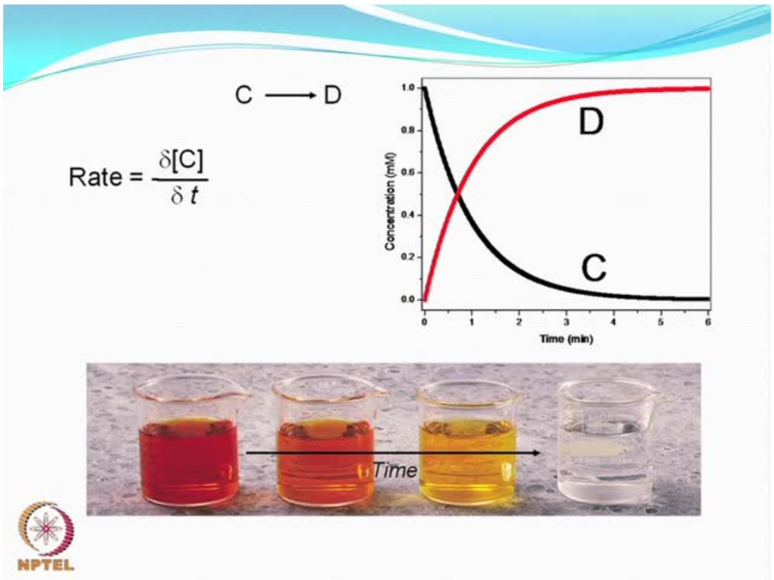

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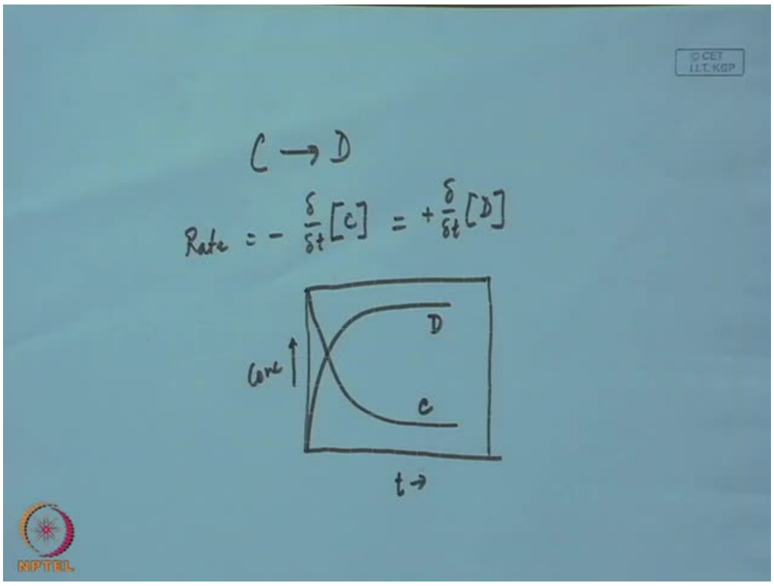

So, let us move on to our next slide, where it is basically the same reaction we just have talked about is your C to D. So, rate is equal to minus of del del t of C, which is equal to plus del del t of D. So, if you plot concentration of C and D together, I mean, in the same graph paper as a function of time, then your D will rise like this and your C will decay like this; so it is C and it is D.

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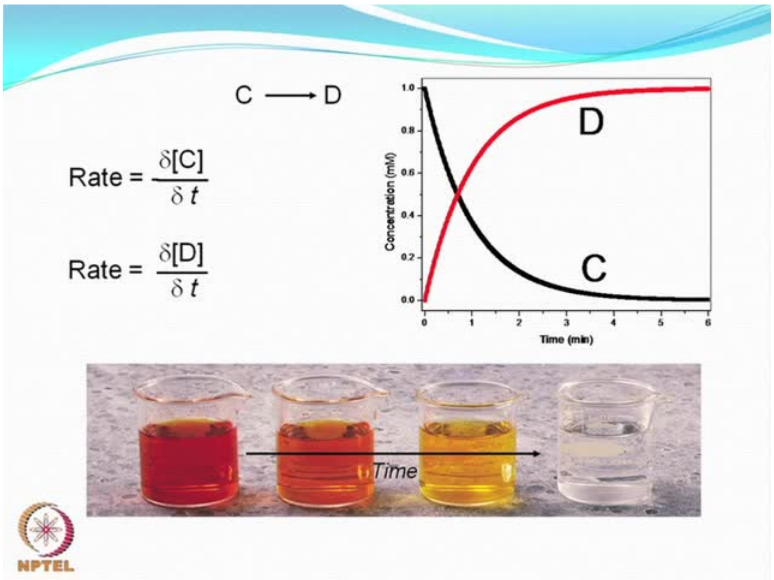

Now, if we look into the slide, that is, you see that, there are four beakers shown over here and you see that the first one is dipped in color, and then, it is fading, it is still fading; now the last one is having no color. So, with time, you see that the color is changing; color is changing means, color is reducing, that is, it is a decolourization reaction, decolourization of a dye with time. You see as time is passed by, color is fading and the reversing may happen, where suppose we are starting from an uncolored or colored substance and in course of reaction, if the color is growing, then opposite trend may be found like it is colorless, then fade color, it is a little deeper and it is the deepest or may be still it will grow with time.

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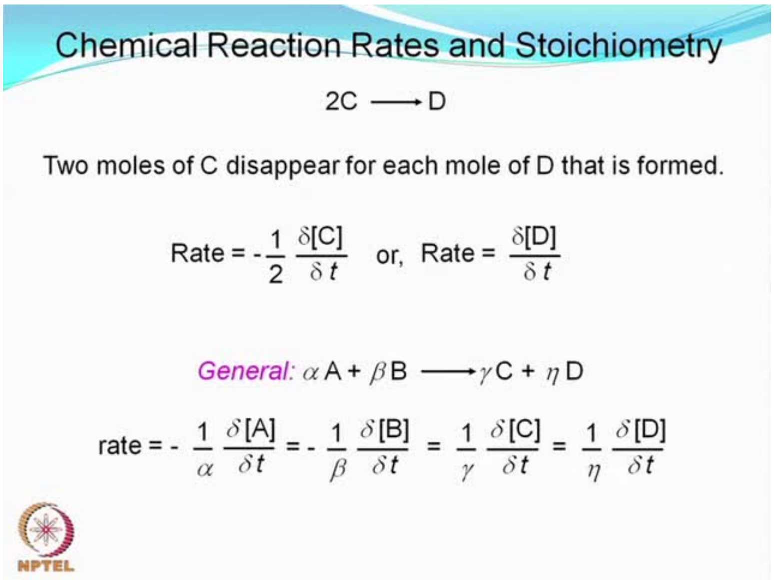

So, let us talk about chemical reaction rate and stoichiometry.

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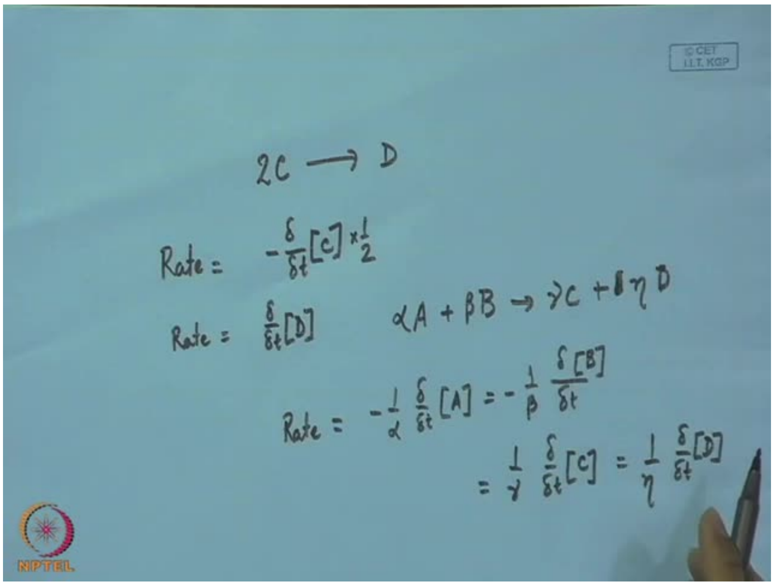

So, start with reaction of this kind, where 2C is converted to D, so that is 2 moles of C is reacting to form the product D. So, how should we write the rate of reaction? Rate will be equal to of course del del t of C with a negative sign multiplied by half Why multiplied by half? into half and also rate can be written as del del t of D. So, why multiplied by half? Because 2 moles are reacting together to produce one mole of D; so to take into account of this stoichiometry, we have to multiply it by 0.5, that is, 1 by 2, because each 2 moles of C together is acting as a single reactant. Therefore, effective concentration of C may be regarded as C by 2 as if 2C, that is, 2 moles of C is forming D that means, it is a bunch of 2C that is why we are dividing it by 2. In general, if we have a chemical reaction like alpha A plus beta B producing gamma C plus delta D, I should not write delta, because I already have used delta, so eta D.

Therefore, rate will be written as, if it is in the reactant, if it is in the form of reactant, then we will put a negative sign; if we write in terms of product and there will be no negative sign; it will be written with a plus sign or without any sign that means, it is a positive quantity. So, that means, rate will be minus 1 upon alpha del del t of A, which is equal to minus of 1 upon beta del del t of B, which is equal to 1 upon gamma del del t of C, which is equal to 1 upon eta del del t of D. So, that means, you see that this alpha, beta, gamma eta, these are all stoichiometric coefficient and this minus sign is for the left hand side, that is, a reactant side and this plus sign or without any sign is for the product side; there is another way we can write the reaction rate.

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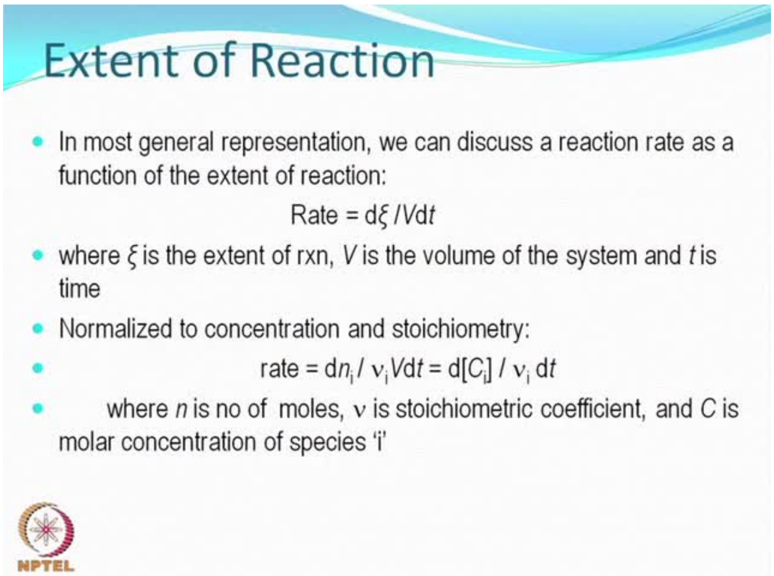

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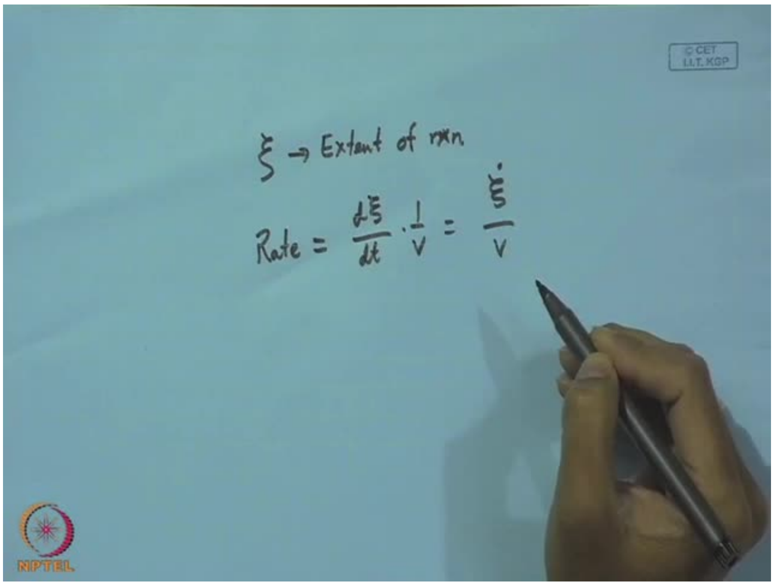

Now, in most general representation, we can discuss reaction rate as a function of extent of reaction; extent of reaction means how many moles of reactant that has reacted. So, in that case we can write if this psi is the extent of reaction, then rate will be written in terms of extent of reaction as follows: d xi dt times 1 upon V. Because suppose if xi moles of reactant have reacted, then and if the total volume is V, then the concentration of your reactant that has reacted is, that is, xi divided by V that is why it is called xi dot by V. So, rate of advancement per unit volume, time rate of advancement per unit volume.

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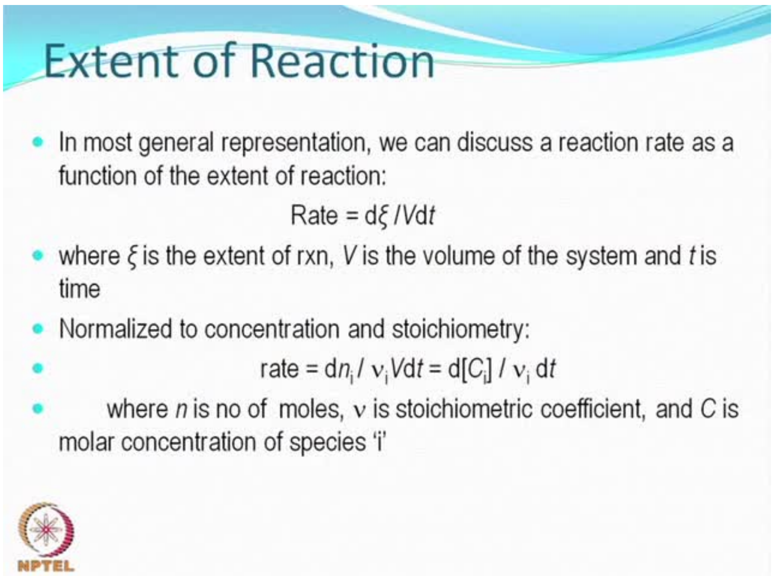

Now, if we normalize it to concentration and stoichiometry, then it may be written as rate is equal to dn i by dt divided by nu i divided by V dt, which is equal to d C i by nu i by dt; so, where n is number of moles, nu is the stoichiometric coefficient, C is the molar concentration of the species i.

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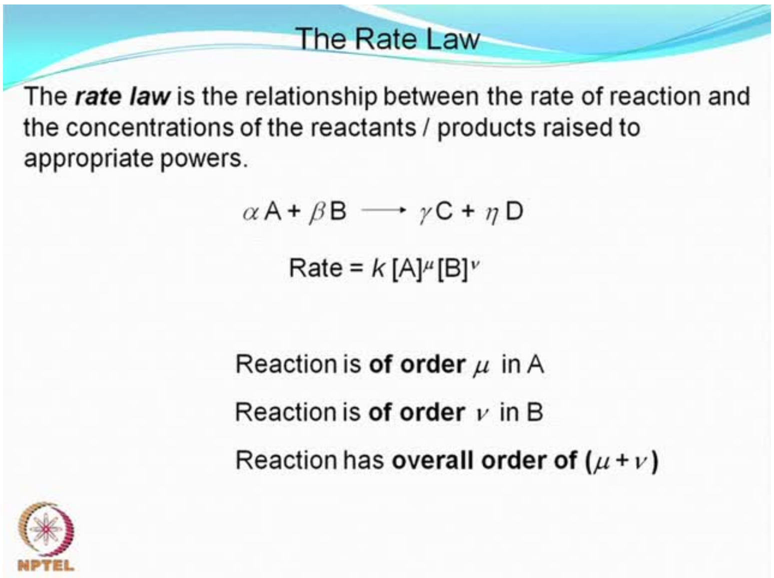

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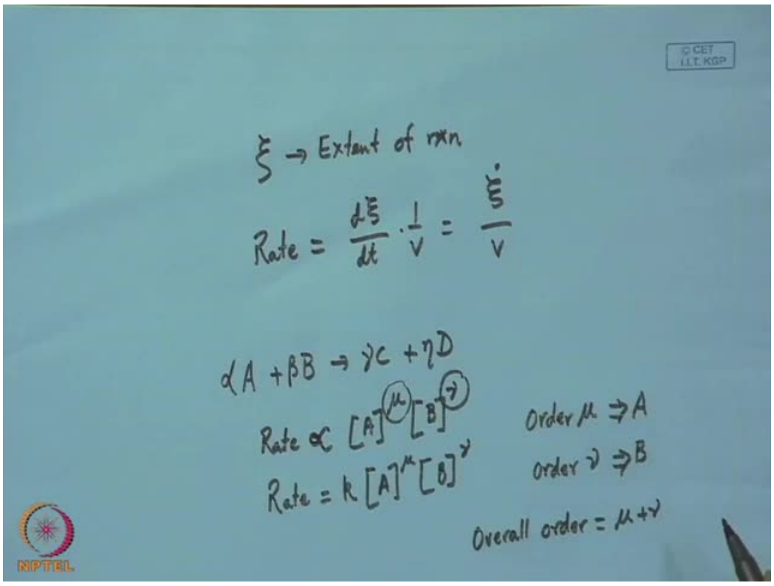

Now, let us move on to rate law. The rate law is the relationship between the rate of reaction and the concentrations of reactant or products raised to the appropriate power. So, consider this reaction alpha A plus beta B producing gamma C plus eta D.

So, rate can be written as say, these are the two reactants; so. If we in generally write rate is equal to or may be written as it is proportional to the concentration of A raised to the power mu and concentration of B raised to the power mu. Because chemical reaction is, I mean, rate of reaction is found to depend on the concentration of reacting species.

S, if we know how this rate is affected with change of concentration of A or with change of concentration of B. So, this is the relation, which talks about how rate is proportional to A and how rate is proportional to B with appropriate power. So, rate is equal to some constant which is called the rate constant, then A to the power mu and B to the power nu. So, that means, we can call that the reaction has order mu with respect to A and order nu with respect to B. So, what is the overall orderable reaction? Overall order will be some of the two individual orders; so, that means, overall order will be equal to mu plus nu.

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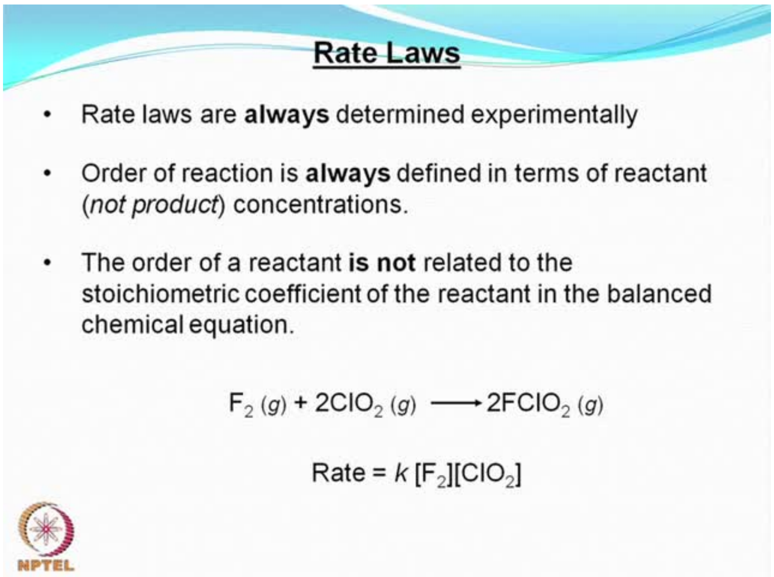

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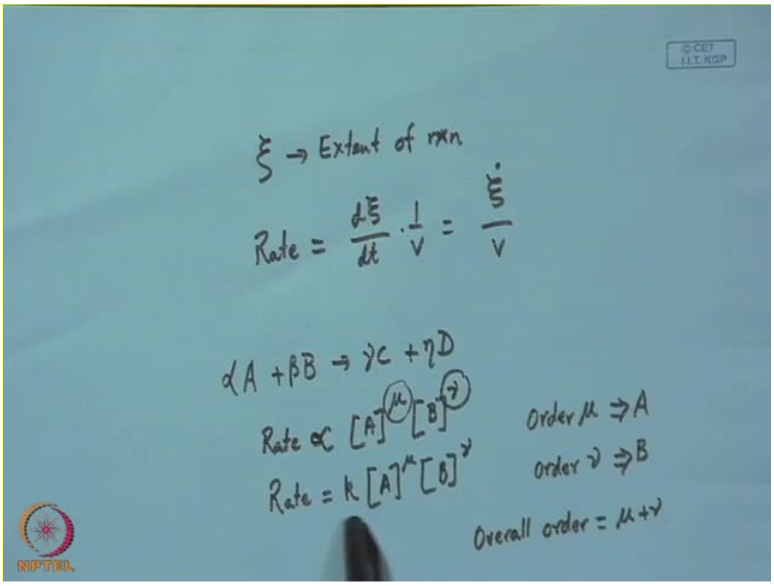

Now, let us move on to rate laws. So, these rate laws are always determined experimentally; so it is nothing but an experimental fact. So, this rate laws that I have written over here. So, this is determined experimental, that means, you change the concentration of A or maybe you change the concentration of B, and then, try to find out or try to formulate a relation between the rate of reaction, that is, rate of appearance or rate of disappearance of some substance as a function of time, and then, you will be able to formulate such a relation. So, this relation means that is called your rate law; so this rate laws are always determined experimentally.

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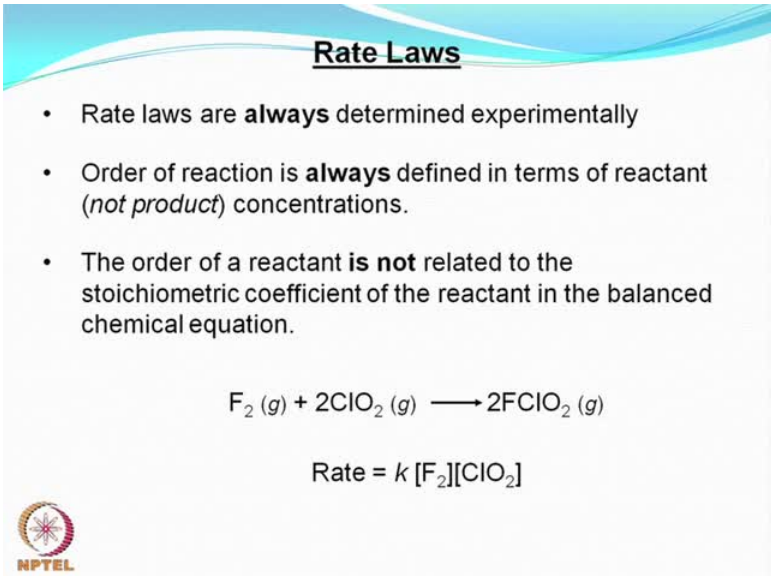

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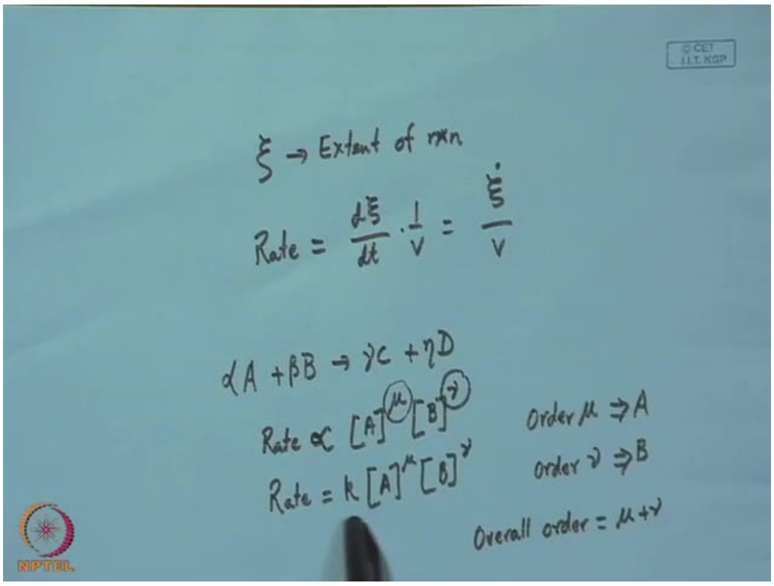

Now, order of reaction is always defined in terms of reactant concentration; not in terms of your product concentration, but it is always defined in terms of reactant concentration. You see that I have written this reaction in terms of order; you see I have written this mu for A, nu for B. So, A B these are these two are all on the left hand side and I have written overall order in terms of their individual contribution towards their total order. So, order of a reaction is always defined in terms of reactant not product concentrations. Next is order of a reaction is not anyway related not anyway related to this stoichiometric coefficient of the reactant in the balanced chemical equation.

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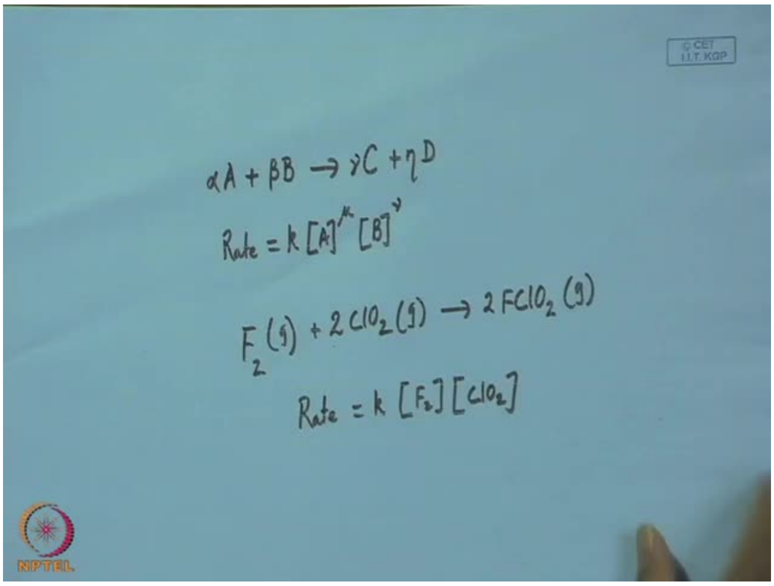

We have to remember this point that, we have got say a chemical reaction of this kind alpha A plus beta B producing gamma C plus eta D. So, rate equation, say rate will be equal to say k I have written earlier, A to the power mu and B to the power nu.

You see, what I mean to say by this, that order of a reaction is not related to stoichiometric coefficient of the reactant in the balanced chemical equation. So, this mu and alpha or may be mu and beta or nu with alpha or nu with beta, there is no relation between them; these are unrelated, these are unrelated event. Because you see that, this order of a reaction it is fully experimentally determined quantity, there is no correlation between the stoichiometric coefficient and this power.

So, let us have an example a concrete example, that fluorine in gas phase reacting with 2 moles of chlorine oxide ClO 2 also in gas phase producing 2 FClO 2 gas. So, here you see that stoichiometric coefficient for fluorine is F 2 is 1; ClO 2 is 2 and FClO 2 is also 2. So, rate is found to depend as follows rate is equal to k times F 2 times ClO 2. Although you see that, this ClO 2 in balanced chemical equation, it has got 2 over here, but you see it is coming as first power. So, that is why there is no relation between this power and this numbers; in some cases, it may so happen that it is an accidental correlation, but it has no physical basis.

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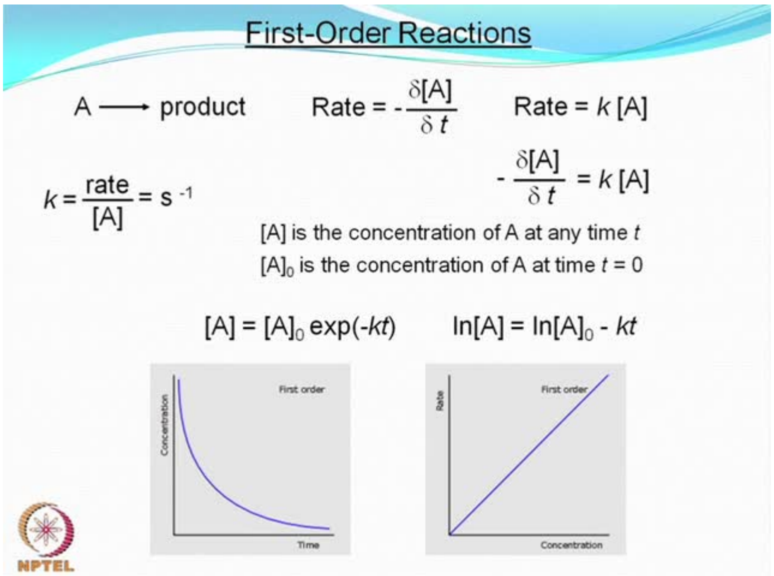

Next is let us move on to first order reaction; so what is the first order reaction?

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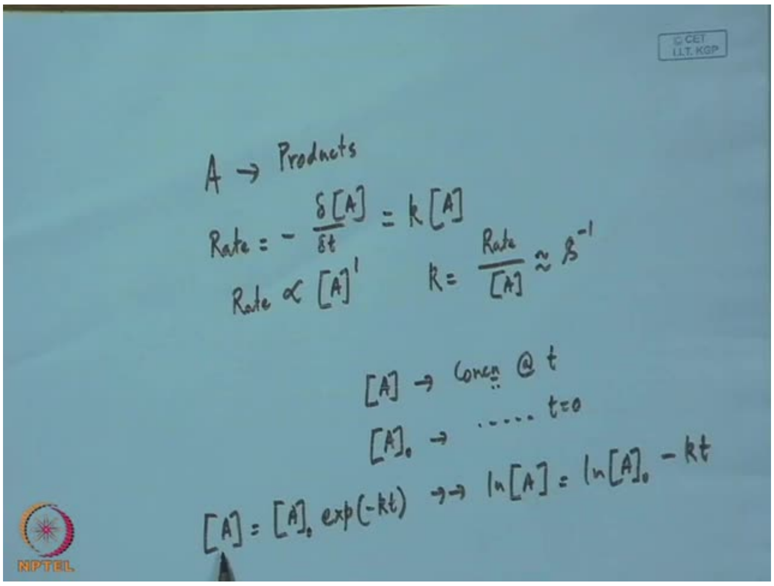

Now, first order reaction is a reaction of this kind, that A, suppose A is producing products, so rate will be written by the following equation, rate is equal to minus d dt of A, because it is depleting therefore, it is a negative sign which is equal to k A, that is, rate is proportional to first power of A; so that is why it is called the first order reaction. So, that means, your rate constant k will be equal to that is,, the dimension will be rate divided by concentration which is nothing but it will be second inverse per second.

Here A is concentration at any time, that is, you know we can write in this way A is concentration at t, and A 0 concentration at t equal to 0, that is, at the starting point of the reaction.

So, if we now integrate, we will be getting like this; exponential it will be an exponential function minus kt or then if we move on to ln, then ln A is equal to ln A naught minus kt.

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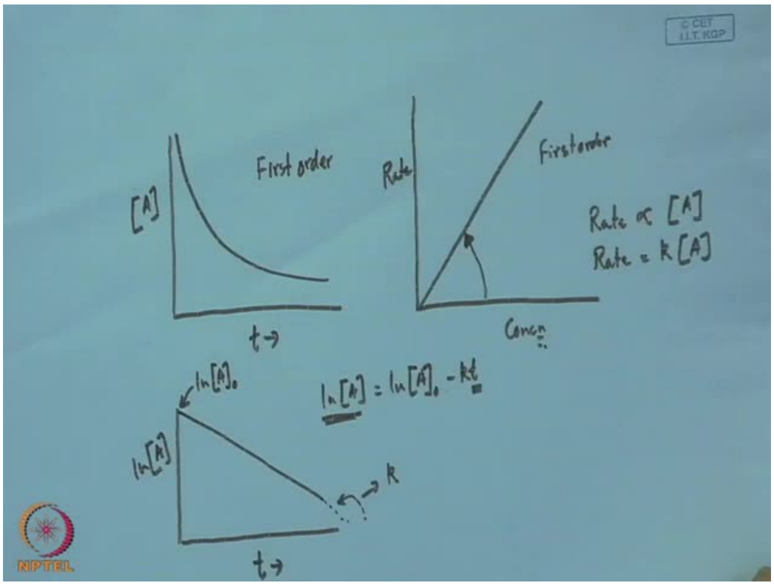

So, you see that, this is your starting concentration, that is, at 0 time when the reaction has not started or just before the start of reaction, this is the concentration of your reactant and this is at any moment of time. So, you see it is in negative sign that means, with increase of time, this quantity will be decreasing; so it is an exponentially decreasing trend. So, if we plot concentration as a function of time, then for the first order reaction, we will be seeing, if we plot as a function of concentration of A, I mean, with time, we will be seeing, it is an exponentially decaying trend; so for first order, it is an exponentially decaying trend.

Now, if we plot, another plot can be possible if we plot rate with concentration; it will be like this for first order that is your rate. Hence, here it is basically rate is proportional to concentration that means rate is equal to some constant into concentration. So, slope will be giving you this k, that is, this side rate; this side concentration; so slope will be giving you k.

Another plot if we do like, if we plot ln A and this side if it is t, then you have to use this equation ln A is equal to ln A naught minus kt. That means, if we plot this ln A with t, then it will have a negative slope with some intercept; so, that means, it will be something like this.

So, this will be your ln A naught and your slope will be, slope is basically it is a negative slope; this is the slope that will give your k rate constant of the processor. For first order, you can have three plots A versus t - concentration versus time, it is an exponentially decaying trend; rate versus concentration, it will have you know just a linear trend and it will start from the origin, because no concentration, there is no reaction; when 0 concentration of reactant, there is no reaction. And there is another plot, that is, if we plot like this ln A as a function of time, then you will be getting this rate constant as also, that is, ln A naught, that is, logarithm of I mean natural logarithm of 0 time concentration of A.

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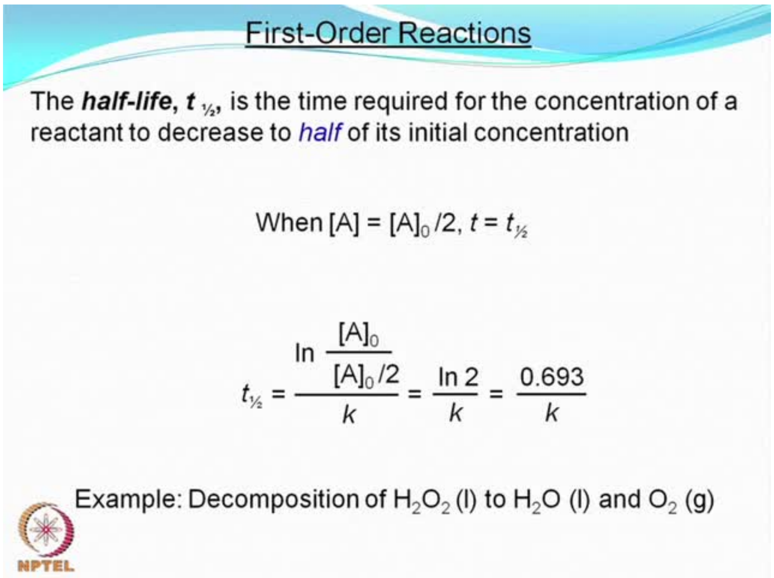

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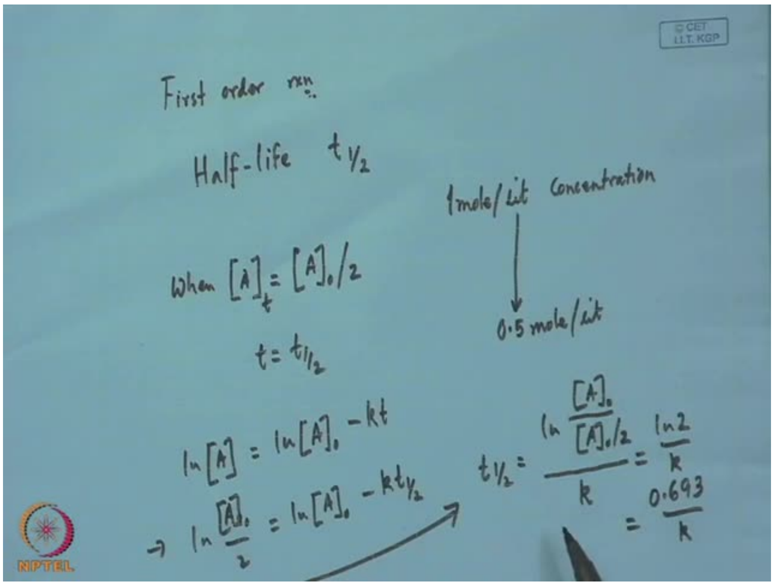

Now, we will move on to another term, which is called half-life, which is for the first order reaction half-life denoted by t half. So, this is nothing but the time required for the concentration of a reactant to decrease to half of its initial concentration.

Suppose we started with 1 mole per liter concentration and suppose after some time the concentration becomes 0.5 mole per liter, then the time required to change the concentration from 1 mole to 0.5 mole is the half-life of the process or the half-life of the reaction involved in such a transformation.

So, we can write when A, that is, A t better to say A t at time t is A 0 or A naught by 2, then corresponding t may be written as t half. So, for the first order reaction, how should we incorporate this t half or how should we calculate t half? So, in that case, we can write ln, let us go back to the logarithmic equation, ln A is equal to ln A naught minus kt. So, A will be as per our requirement; A will be this A will be 0 by 2; so let us put ln A 0, that is, A naught by 2 is equal to ln A naught minus k t half. So, from this, we can write t half is equal to ln A 0 by A 0 by 2 divided by k; basically this is equal to ln 2 by k, which is nothing but equal to 0.693 by k.

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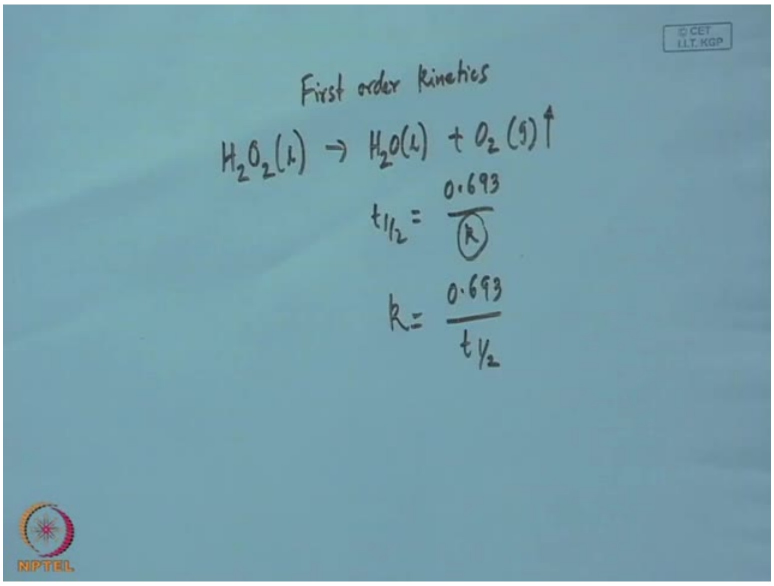

So, you see that for the first order reaction it is 0.693 by k. So, this happens also in case of radioactive disintegration, where the process occurs via your first order kinetics, that is, the radioactive disintegration occurs via first order kinetics. So, a typical example for such a first order process may be like decomposition of your H2 O 2 to water plus oxygen in gas phase.

So, this follows a first order kinetics, that means, t half will be whatever k will be getting that will be using this 0.693 by k. So, if we measure if we can measure t half, then it is possible to find out this k, that means, t half means the time required for the initial concentration of H 2 O 2 to decay to reduce to half, that time is here we will put that value, and then, right hand side will be 0.693 by k; so k will be equal to 0.693 by t half. So, k will be equal to 0.693 by t half; so in this, we can also find out the rate constant.

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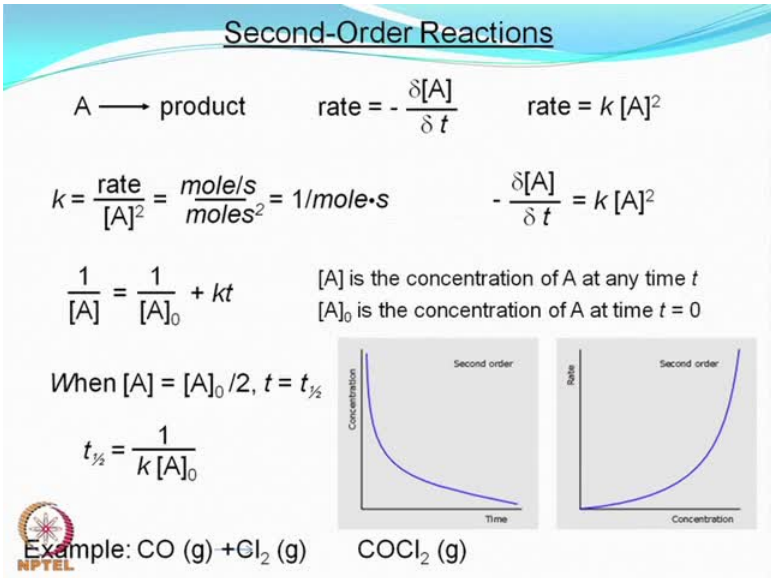

Now, we will move on to second order reaction. So, we have just finished the first order; next, we will move on to second order.

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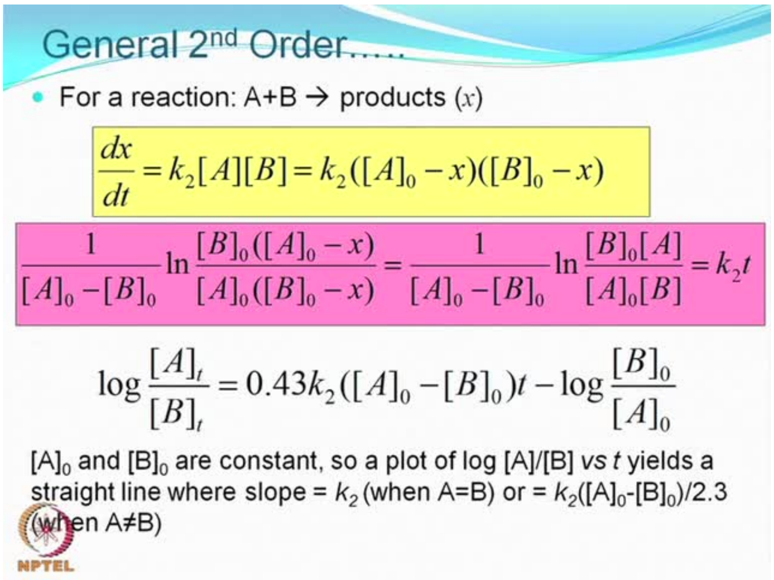

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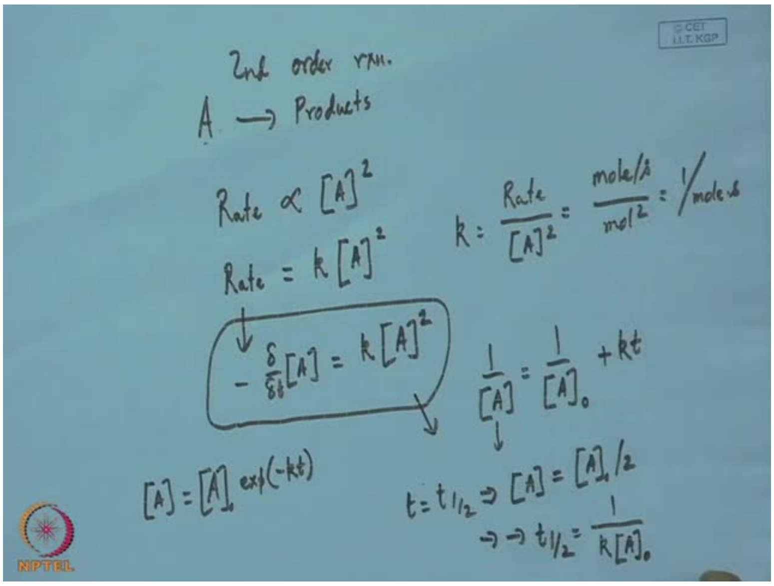

So, for second order reaction typically your rate equation will be like A giving rise to products; so it is a second order reaction. So, rate, very simply you can write rate is proportional to concentration of A to the power 2. So, that means, rate will be equal to k into A square. Now, rate is nothing but equal to this is nothing but equal to minus of del del t of A, which is equal to k into A square. So, it is a simple secondary reaction, where the same molecule of A is taking part.

There are examples, where say A plus B giving rise to products and that is found to follow a second order kinetics that is also there, but it is a simple simplified case; so that means this is the rate equation.

Now, k will be equal to rate divided by A square, that is, your mole per second divided by mole square, that is, 1 by it will be 1 by mole second; of course, per liter is there always, because concentration has got mole per liter, so mole means mole per liter.

Now, if we integrate this one, this if we integrate this differential equation, we will be getting 1 by A is equal to 1 by A 0 plus kt. So, recall your first order kinetics, so what you got there? that your That it is basically and exponentially decaying kinetics, that means, A is equal to A 0 exponential minus kt. So, there is a huge difference in terms of your integrated equation.

So, there is a huge difference. So, we will discuss how this plot will look like. So, this is your concentration at any time; this is your 0 time concentrate, that is, when t equal to 0 that is at the start of the reaction.

Now, if we think of the t half, then how should we calculate t half? That is when t is equal to t half, then your A is nothing but A 0 by 2. So, from this, we can write that t half is equal to 1 by k into A 0. So, t half you see that, t half is inversely related to the initial concentration of the reactant.

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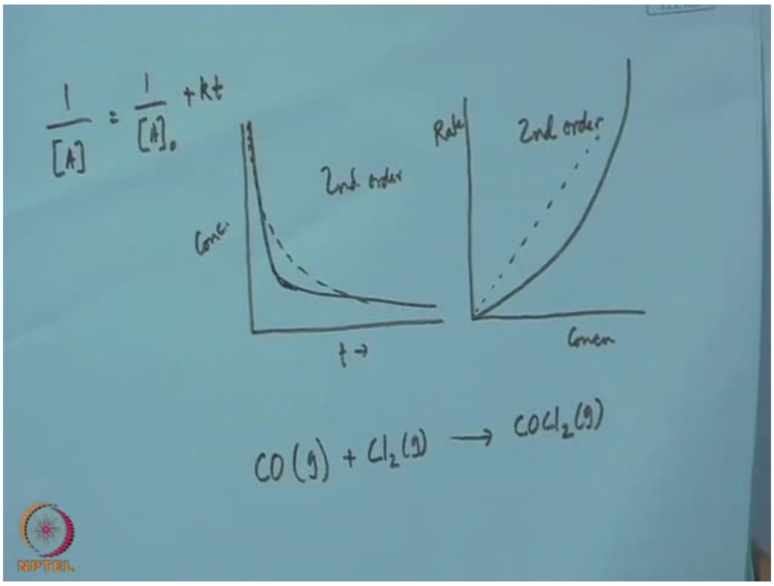

Now, let us move on to plots for a second order reaction the integrated equation is like 1 by A is equal to 1 by A naught plus kt. So, if we plot now like concentration versus time, it will not be an exponential rather it will be something like this; some kind of hyperbolic nature, so it is a second order.

So, you can have a look at the slide also and if we plot rate and versus concentration, then it will be, there is a growing trend; so it is growing up. So, typical example could be, it is a typical example CO gas plus Cl 2 gas producing COCl 2 gas; so this follows your second order kinetics.

So, for you see that, for your first order case, it was an exponentially decaying trend, but here it is not an exponentially decaying trend, but it is a hyperbolic dependence or may be it is not an exponential one; it is something different as you if we look into this graph, and also rate versus concentration, if we plot rate versus concentration for your first order, it is a straight line like this for your first (( )) was straight line, but you see it is growing up; it is an upward curvature. So, by looking at the concentration versus time plot or may be rate versus concentration plot, we can in principle, distinguish between a first order and a second order reaction.

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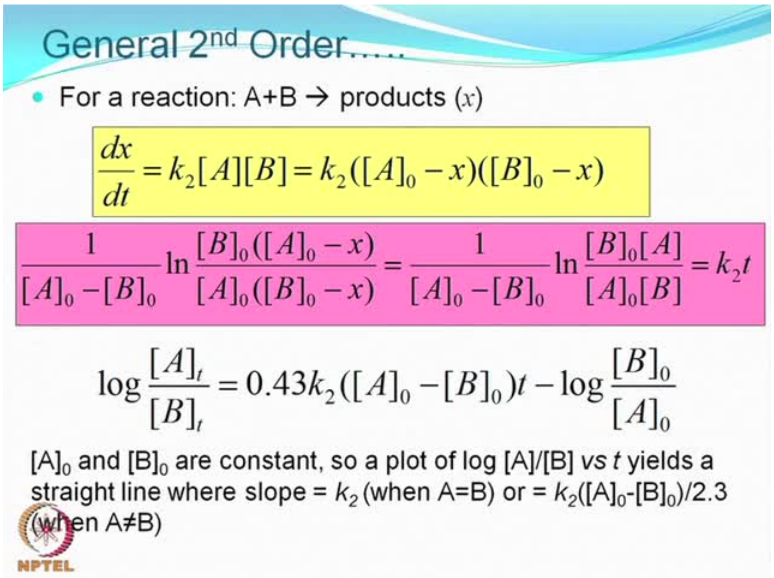

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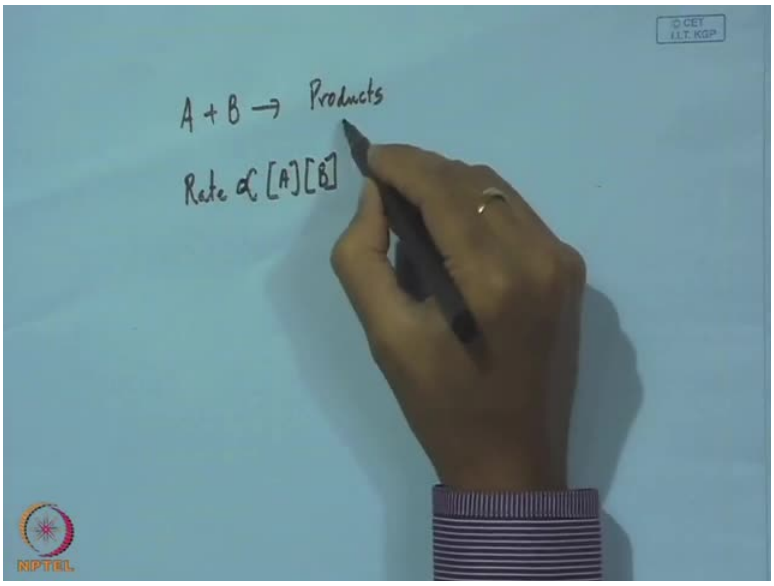

Now, general second order reaction, that is, A plus B producing products. So, general second order reaction means your rate will be equal to or I mean proportional to concentration of A concentration of, although I have started with a discussion, where your second order reaction was a simple case, where rate was proportional to say concentration of a whole square.

Now, we are we are talking about rate, which is proportional to product of concentration of A and concentration of B and in both cases, their power is 1, that is, why it is a second order kinetics.

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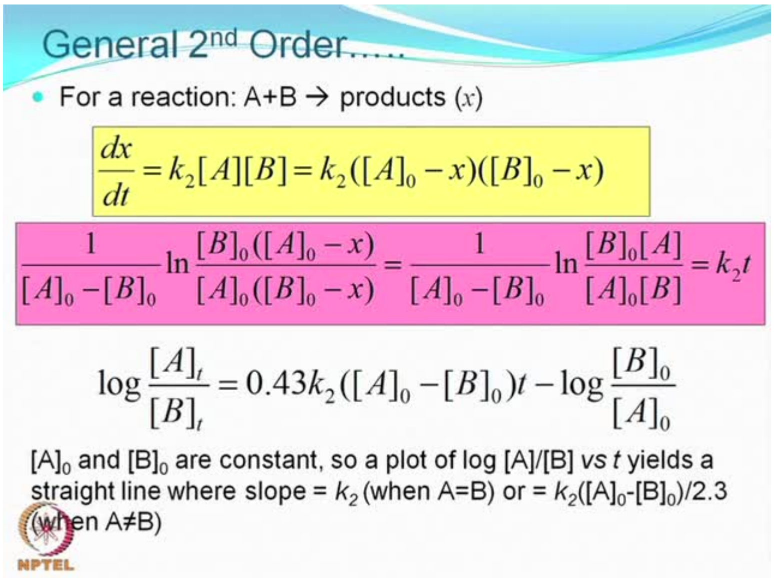

So, your rate equation looks like this, dx dt, that is, x if the concentration of product is x, then dx dt is equal to k 2, because it is a second order reaction that is why I have written k 2 A B. So, then I can write k 2 times A naught minus x, where this is your amount of product that is formed and this is your initial concentration of A. So, therefore, this much that is A naught minus x is the amount of A, I mean, concentration of A remaining in the same way B naught minus x is the concentration of B, that is, remaining at a certain instant and upon integration, we end up to this expression like this.

And if we finally, I mean, modify it properly, then it looks like logarithm of A by B at the instant of t, which is equal to 0.43, then rate constant times A naught minus B naught into t minus log B naught by A naught, and this B naught and A naught, that is, B 0 and A 0, these are the constants.

So, that is why if we plot the left hand side as a function of t, I mean, x axis t y axis log A by B, then it will be giving you a straight line and a slope will be giving means from the slope, we will be getting your rate constant. So, this is a general second order reaction; for this, we can write like this.

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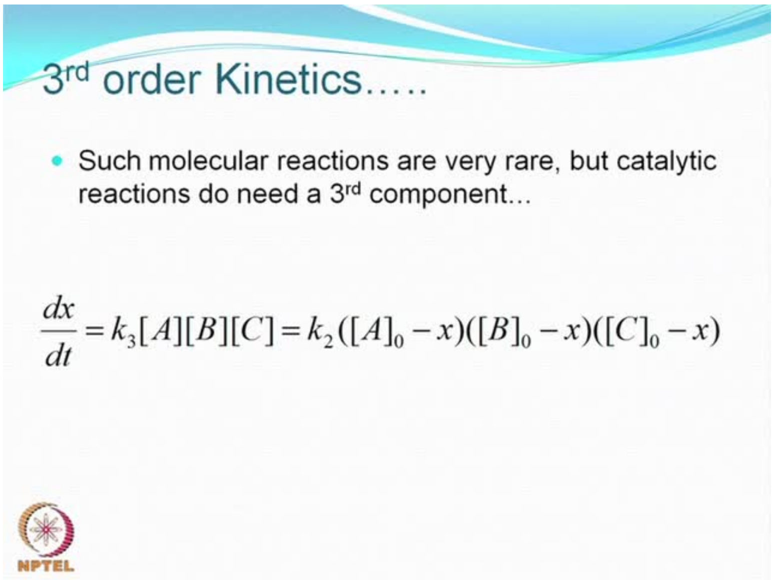

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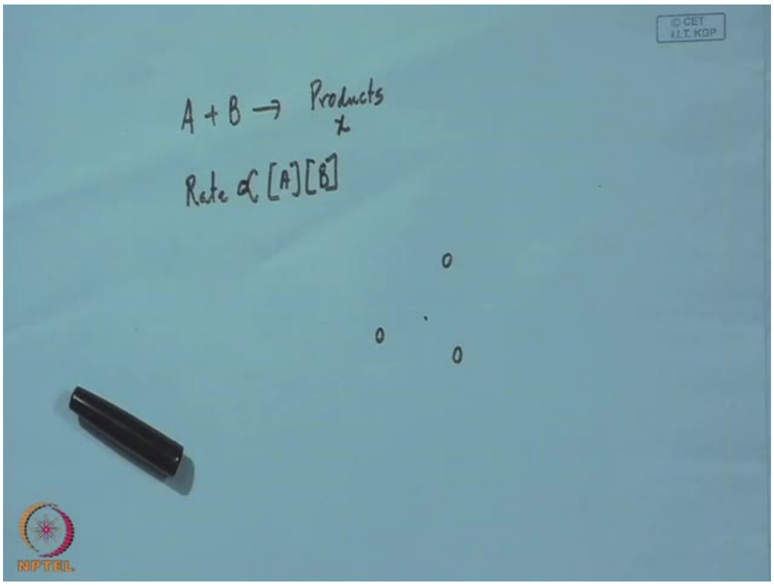

What about third order reaction? Still third order reaction is a possibility that second order reaction, for second order reaction to happen like say 2 dissimilar substances, then according to the latest theory of reaction rate, we can say that there is a requirement of collision between A and B to form the product. So, that means, for a two body collision, that is, A and B, collision between A and B, it is possible. But suppose a three body collision, that is, you have got one particle over here, another particle over here and the third particle over here and these two three particle will meet at one point, at the same time is a very rare event that is why third order kinetics for which three body collision is a requirement and now such molecular reactions are very rare, although catalytic reactions do need a third component and in that case for a third order kinetics, your rate expression will look this.

For a general third order kinetics, the rate expression looks like this, that is, you know dx dt is k 3 is for the third order kinetics; A, B, C and this is concentration of A after you know certain time t; it is concentration of B after certain time t and concentration of C after certain time t.

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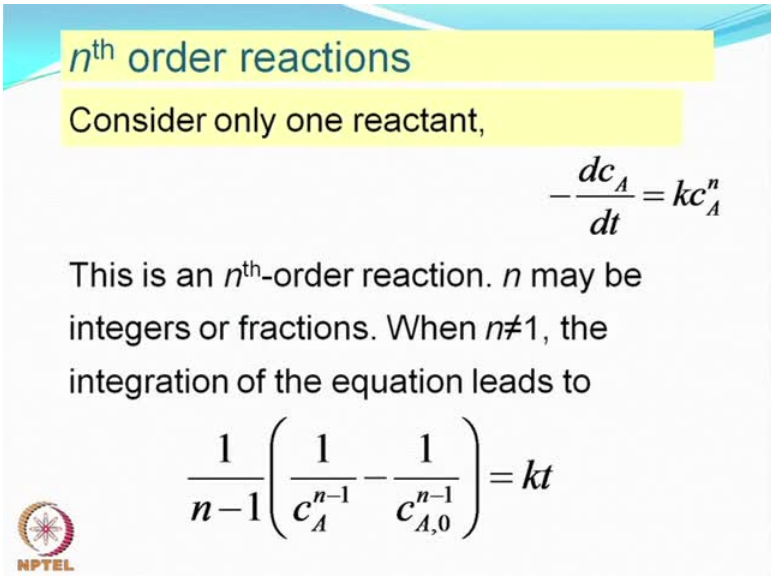

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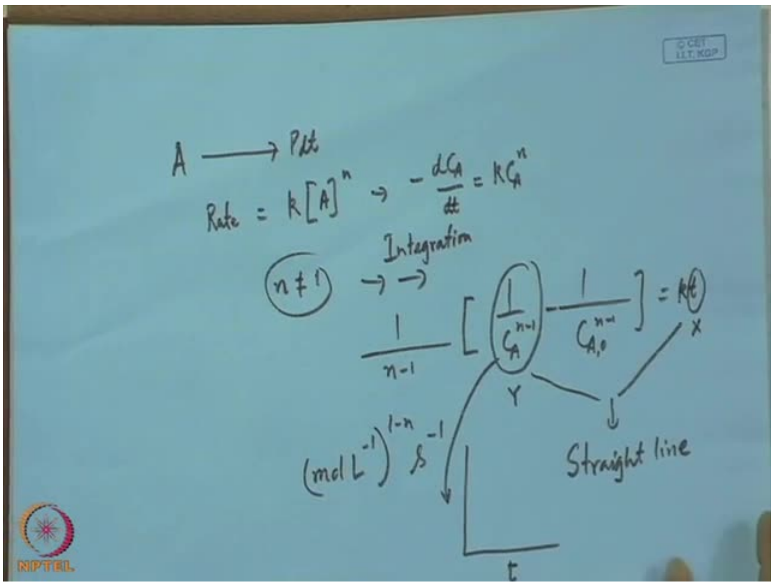

What about n th order reaction? It is the general expression, so if we consider only one reactant, that is, only one reactant producing only one reactant producing product, so say A product. So, in that case, for a general n th order reaction, rate will be equal to k to the power n, that is, n th power; it rate depends on the n th power of A, that is, minus dC A dt is equal to kC A concentration of A to the power n.

Now, n may be n can be integer; in certain cases n is found to be fraction; I will come to this point on the fractional value of n. So, that is a special case that is fractional order and certain cases, it is found that reaction is following a fractional order although stoichiometry is not fraction, but reaction is found to follow the fractional order.

So, that is a separate issue, but right now when n is now, if we concentrate on to this expression, when n is not equal to 1 that is not for the first order case and if we think that n is not equal to 1 and if we integrate the expression, upon integration we get this expression n minus 1 times 1 by C A to the power n minus 1 by C A 0 n minus 1 which is equal to kt.

So, if n is equal to 1, then this will have no meaning that is why when n is not equal to 1, that is, the requirement we can integrate this expression. So, what are the features of this n th order reaction? Now, the unit of k will be like mole liter inverse to the power 1 minus n second inverse and also if we plot this as a function of t, then this together will be giving you a straight line, that is, if we plot this in Y axis and this in X axis, then this plot will be a straight line. So, with time it will follow a strict kinetics, so if we plot here this one and this one over here, then it will be a straight line.

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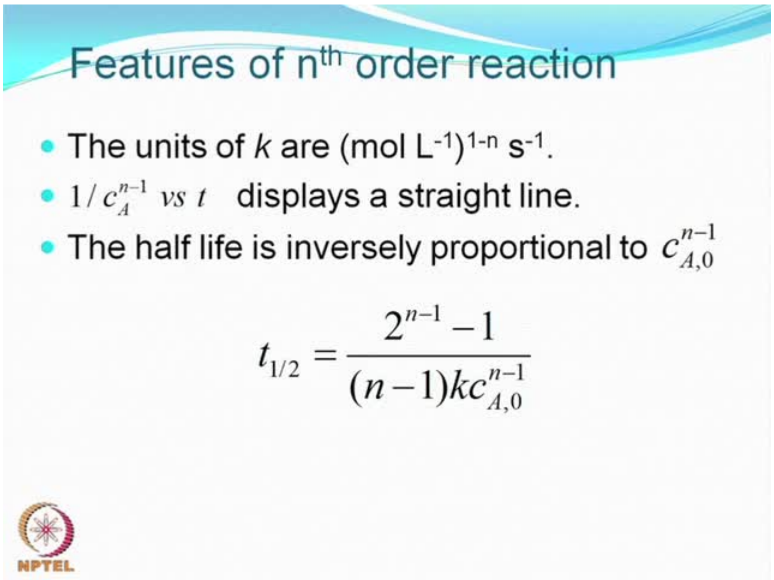

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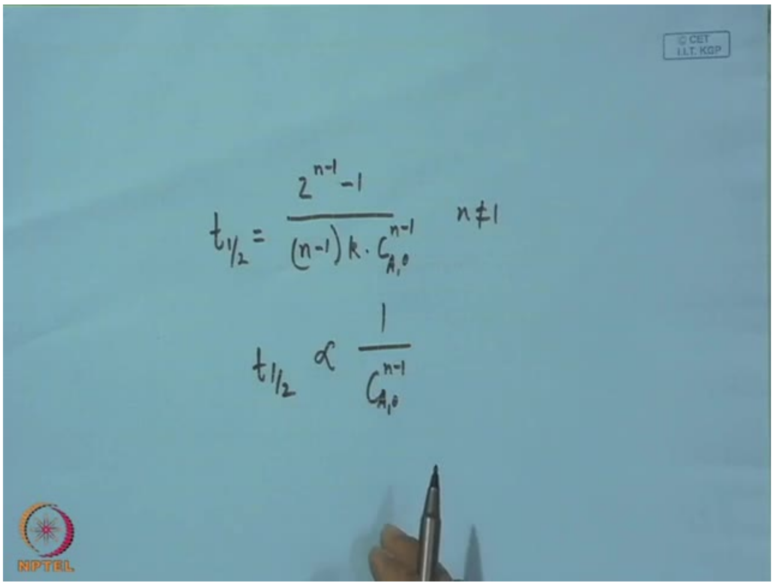

And t half will be, for a general n th order reaction, t half will be equal to 2 the power n minus 1 minus 1 divided by n minus 1 k into C A 0 n minus 1 of course, n is not equal to 1. You see that for the n th order reaction, it will be proportional to 1 by the initial concentration of the reactant raised to the power n minus 1, that is, t half will be proportional to 1 by C A 0 n minus 1.

So, this is the t half value for a general n th order reaction of course, when n is not equal to 1; otherwise, if n is equal to 1, then again we will have a problem that will be meaningless.

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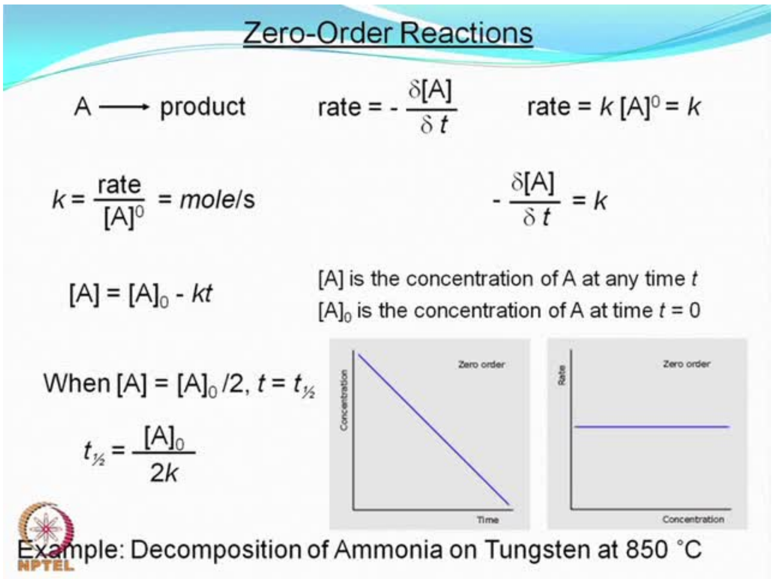

Now, let us move on to an interesting thing which is called the zero-order reaction, so what is that zero-order reaction?

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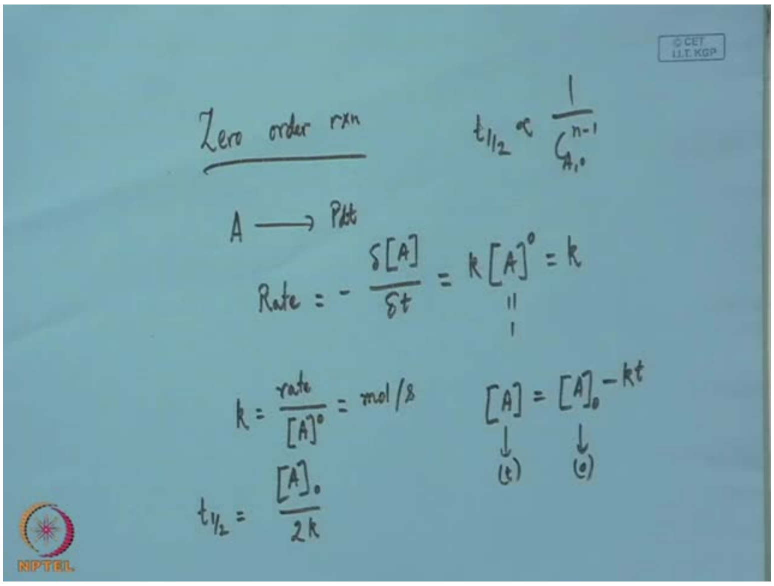

Zero-order reaction- So, reactant, product. Rate, let us write rate is equal to minus delta t that is equal to k rate constant times A to the power 0. So, this means equal to 1, so that is equal to k. So, that means rate is independent of concentration of your reactant.

So, that means, in that case, k will be rate divided by rate divided by A to the power 0 moles per second. So, that means, if we integrate this expression, we will be getting A is equal to A naught minus kt; so that means this is at any time t, this is at time 0.

So, then what is the value of t half? So, t half will be equal to A 0 by twice k; so you see that it depends on the first power of A. So, recall a general n th order reaction, where we have written t half is proportional to 1 by C A 0 to the power n minus 1. So, if we put n is equal to 0, then this part will move on to over here, that is why t half is proportional to this, I mean, these two match quite well.

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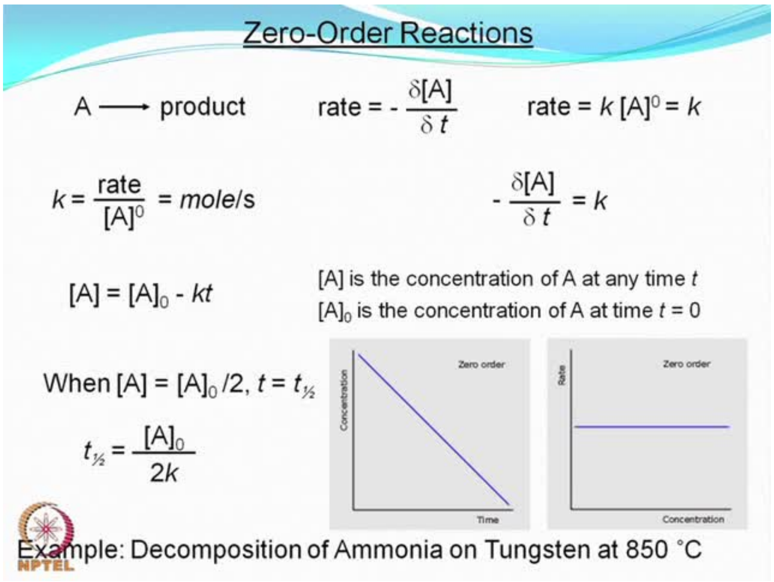

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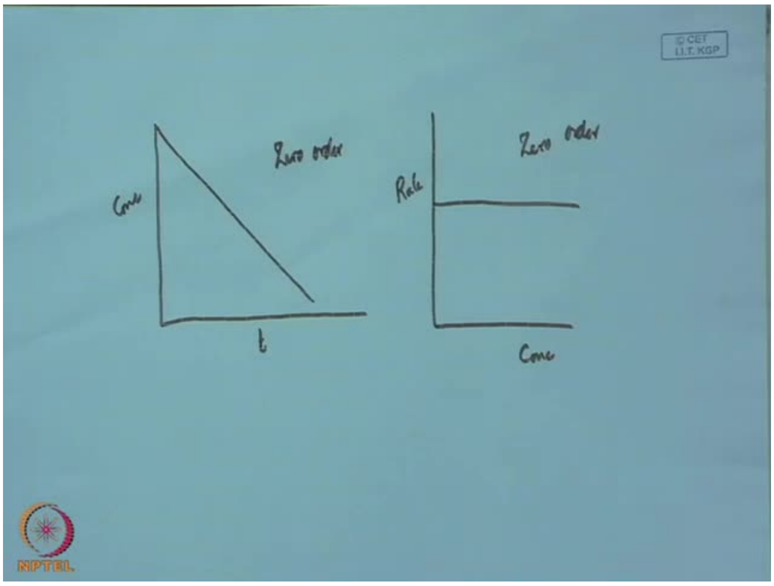

Now, if we have a plot like concentration versus time, then for a zero order reaction, it will be like this, rate versus concentration, it will be flat zero order.

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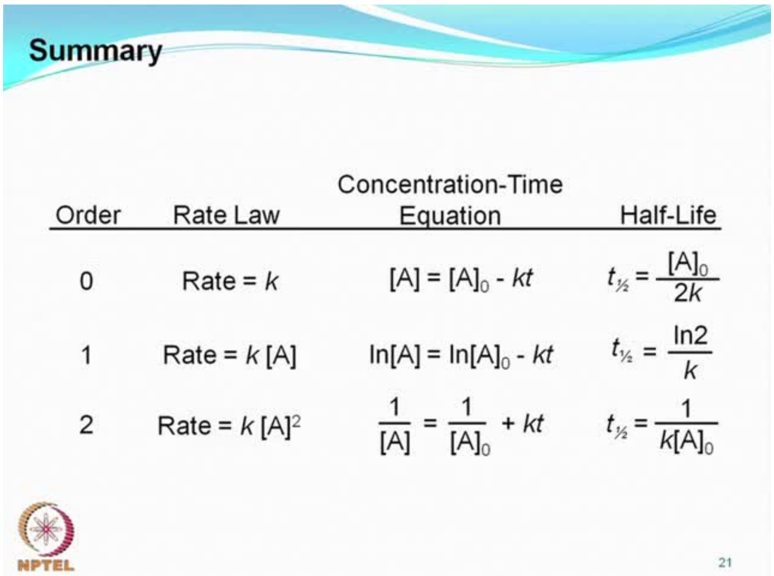

So, typical example will be decompensation of ammonia on tungsten or gold surface at an elevated temperature are the examples of zero order kinetics.

So, in summary what we have learnt up to now? That kinetics deals with how fast a chemical reaction proceeds with time, but thermodynamics talks about the feasibility. So, although in certain cases, it has been found that certain substances are thermodynamically unstable, but it is found that they are still existing; it is because of the fact that, they are kinetically stable. Stable means, their reactions are very slow and in some in other cases, some substances are found that they are although thermodynamically stable, but kinetically unstable, that means, that substance is also undergoing reaction very fast.

So, that means, thermo although thermodynamic stability is good, but kinetic stability less means, it is reacting fast; thermodynamic stability less, kinetic stability high in that case, the reaction will also I mean the substance will also be stable. So, that is very important point. Now, we have also learnt this rate laws; in this case, that we have we have seen order can be zero order, first order, second order and rate equations are like for z order, rate is k; first order, rate will be equal to k times A; second order, k times A square. And their half-life's are basically you know for zero order, it is proportional to the A 0 to the power of 1; for first order, it is independent of A 0; for the second order, it is inversely proportionally to the first power of A 0.

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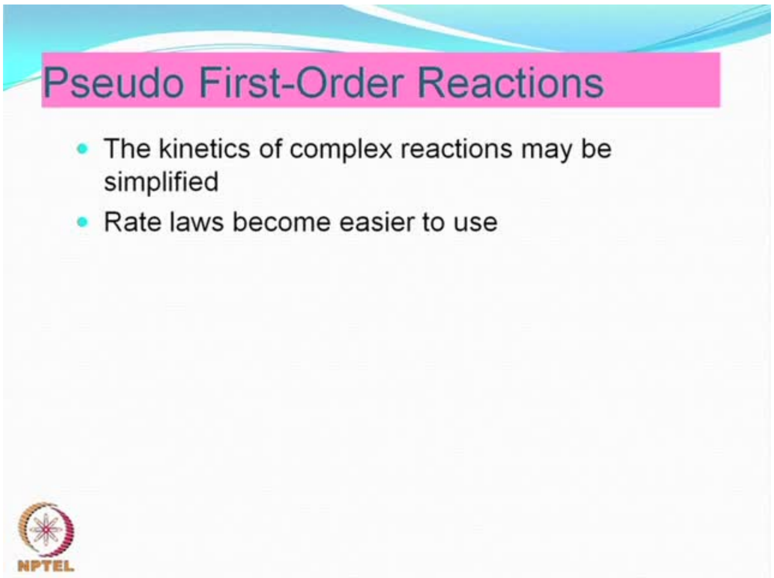

So, we learnt this basic rate laws and their corresponding equation and half-life and also the importance of kinetics you know, how this can be applied to further cases. You know, in next couple of classes, we will talk about other things, but in the next class, we will talk about a little complicated reactions like pseudo order reaction, that is, although a reaction is second order, but under certain circumstance, this substance maybe appearing to us like reacting in a first order kinetic. So, we will talk about this pseudo order reaction and also how this reaction rates can be measured, we will talk about a little bit or may be in a little in next class till then goodbye.